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BIOFILTRATION D'UN MÉLANGE DE MÉTHANE ET DE STYRÈNE DANS DES BIOFILTRES INORGANIQUES EN PRÉSENCE D'UNE SOLUTION NUTRITIVE RECYCLÉE

Biofiltration of methane and styrene mixtures in inorganic biofilters with recycled nutrient solution

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To my mother …

Dans le cadre de la présente activité pédagogique, j'ai pris connaissance de la déclaration d'intégrité relative au plagiat disponible sur le site du Service de soutien à la formation, section antiplagiat.

Bahman Khabiri

RÉSUMÉ

Le méthane (CH_4), important gaz à effet de serre (GES), a des effets néfastes sur l'environnement en raison de son potentiel de réchauffement global (PRG). Toute mesure conduisant à une réduction des émissions de CH_4 mérite d'être encouragée afin de limiter les effets du changement climatique sur la planète. Le procédé de biofiltration est une approche prometteuse pour l'élimination des émissions de CH_4 (concentrations inférieures à 5% v/v). Les micro-organismes, contenus dans le biofiltre, ont besoin de nutriments supplémentaires, qui sont généralement ajoutés sous forme d'une solution nutritive (NS). L'excès de NS, quittant le biofiltre sous forme de lixiviat, doit être traité dans des stations de traitement des eaux usées (STEP). Le méthane émis par les stations d'épuration, les sites d'enfouissement, les raffineries et les complexes pétrochimiques peut être accompagné de composés aromatiques tels que des vapeurs de styrène (C_8H_8). Le styrène est un composé cancérigène qui doit être traité comme un gaz résiduel. La présence d'un mélange de CH_4 et de C_8H_8 dans un biofiltre peut entraîner certaines limitations dans les performances du bioprocédé, en raison des effets inhibiteurs du C_8H_8 sur la biodégradation du CH_4. L'objectif principal de cette étude est de réduire la production de lixiviat et d'examiner la capacité du procédé de biofiltration lors du traitement d'un mélange de CH_4 et de C_8H_8. Premièrement, une revue de la littérature a été effectuée sur la production de CH_4 dans les stations d'épuration et les réseaux de canalisation des eaux usées, en tant que source mondiale croissante d'émissions de GES, et sur les approches potentielles permettant la bioélimination du CH_4. Deuxièmement, deux biofiltres de 18 L (B1 et B2) remplis d'un garnissage inorganique ont été exploités pendant 283 jours sous un temps de résidence en fût vide (EBRT) constant de 6 min et des charges à l'entrée (IL) de CH_4 de 7 à 63 g m^{-3} h^{-1}. Le biofiltre B1 a été alimenté avec une NS fraîche chaque jour et B2 a été entretenu avec une NS recyclée à partir d'un réservoir de 10 L afin de réduire l'utilisation de NS (les deux biofiltres ont été alimentés avec 2 L d^{-1} de NS, débit volumique de 1 L min^{-1}). Une conversion maximale de CH_4 de 66% (IL de 13 g m^{-3} h^{-1}) pour B1 et de 67% (IL de 30 g m^{-3} h^{-1}) pour B2 a été observée. Troisièmement, quatre biofiltres à flux ascendant également remplis d'un garnissage inorganique ont été étudiés à un débit d'air constant de 3 L min^{-1} pour examiner l'effet du C_8H_8 sur la biofiltration du CH_4. Différentes ILs de CH_4, variant dans une plage de 7 à 60 g m^{-3} h^{-1}, ont été évaluées dans ces biofiltres en utilisant des ILs constantes de C_8H_8 (B-ME (C_8H_8 IL de 0 g m^{-3} h^{-1}), B-200 (C_8H_8 IL de 9 g m^{-3} h^{-1}), B-500 (C_8H_8 IL de 22 g m^{-3} h^{-1}) et B-700 (C_8H_8 IL de 32 g m^{-3} h^{-1})). Les biofiltres ont été irrigués avec une NS recyclée (débit de 1 L min^{-1}) à partir d'un réservoir de 20 L. Des conversions de C_8H_8 variant entre 64 et 100% ont été obtenues en augmentant les ILs de CH_4 et de C_8H_8 de 7 à 60 g m^{-3} h^{-1} et de 0 à 32 g m^{-3} h^{-1}, respectivement. Plus de 90% du C_8H_8 a été éliminé dans les sections basses et centrales des biofiltres. Une étude macro-cinétique basée sur le modèle de Michaelis-Menten a confirmé qu'une inhibition non compétitive s'est produite lors de la biofiltration du mélange CH_4+C_8H_8.

Mots-clés: Gaz à effet de serres, Eaux usées, Procédé de biofiltration, Méthane, Styrène, Solution nutritive.

ABSTRACT

Methane (CH_4), as an important greenhouse gas (GHG), has harmful effects on the environment due to its global warming potency (GWP). Any effort leading to a decline in the emission of CH_4 could be a worthy step in order to prevent the planet's climate change. Biofiltration process is a promising approach for CH_4 elimination (concentrations below 5% v/v). Microorganisms in a CH_4 biofilter need supplementary nutrients, which are usually added as a nutrient solution (NS). The excess NS leaves the biofilter as leachate, which has to be treated in wastewater treatment plants (WWTPs). Methane emitted from WWTPs, landfills, refineries and petrochemical complexes could be accompanied by aromatic compounds such as styrene (C_8H_8) vapors. Styrene is a carcinogenic compound and should be treated as a waste gas. Presence of CH_4 and C_8H_8 as a mixture in a biofilter may result in some limits for the bioprocess's performance, due to the inhibitory effects of C_8H_8 on CH_4 biodegradation. The main objective of this study is to reduce the production of leachate and examine the capability of biofiltration process when treating a mixture of CH_4 and C_8H_8. Firstly, a literature review was provided on the production of CH_4 in WWTPs and sewer networks, as a growing worldwide source of GHG emission, and on the potential approaches for CH_4 bioelimination. Secondly, two 18 L biofilters (B1 and B2) packed with inorganic materials were operated for 283 days under a constant empty bed residence time (EBRT) of 6 min at CH_4 inlet loads (ILs) of 7 to 63 g m^{-3} h^{-1}. Biofilter B1 was fed with a fresh NS every day and B2 was fed with a recycled NS from a 10 L tank in order to use less NS (both were supplied with 2 L d^{-1} NS, flow rate of 1 L min^{-1}). Maximum CH_4 removal efficiency (RE) of 66% (IL of 13 g m^{-3} h^{-1}) for B1 and 67% (IL of 30 g m^{-3} h^{-1}) for B2 was observed. Thirdly, four upflow biofilters also packed with inorganic materials were operated at a constant airflow rate of 3 L min^{-1} to examine the effect of C_8H_8 on the CH_4 biofilters. Different CH_4 ILs varying in the range of 7 to 60 g m^{-3} h^{-1} were evaluated in biofilters with constant flow of C_8H_8. B-ME (C_8H_8 IL of 0 g m^{-3} h^{-1}), B-200 (C_8H_8 IL of 9 g m^{-3} h^{-1}), B-500 (C_8H_8 IL of 22 g m^{-3} h^{-1}) and B-700 (C_8H_8 IL of 32 g m^{-3} h^{-1}) were irrigated with recycled NS (1 L d^{-1}, flow rate of 1 L min^{-1}) from a 20 L tank. The C_8H_8 REs varying between 64 and 100% were obtained at CH_4 ILs increasing from 7 to 60 g m^{-3} h^{-1} and for C_8H_8 ILs range of 0 to 32 g m^{-3} h^{-1}. More than 90% of C_8H_8 was removed in biofilters' bottom and middle beds. A macrokinetic study based on the Michaelis-Menten model confirmed that an uncompetitive inhibition occurred during CH_4+C_8H_8 biofiltration.

Keywords: Greenhouse gas, Wastewater, Biofiltration process, Methane, Styrene, Nutrient solution.

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CHAPTER 1 Introduction

Methane (CH_4) as the second most important greenhouse gas (GHG) leads to global warming, which ends up with climate change, a dangerous phenomenon for the planet. A global consensus of the United Nations Framework Convention on Climate Change (UNFCCC), from France COP21 (2015) to Spain COP25 (2019), aimed to reduce GHG emissions in favor of restricting the global warming to 2ºC between 1800 and 2100 [1, 2]. Methane emissions have increased since preindustrial times and continue to rise rapidly [3]. Following a very slow increase during preindustrial years (0.04 ppbv per year), atmospheric CH_4 concentration increased significantly by 4 ppbv annually, between 1750 and 1990 [4, 5]. A massive annual increase of 8 ppbv starting in 2007 led to a CH_4 atmospheric concentration of 1866 ppbv in 2019 [3, 6].

In Canada, total GHG emissions increased from 602 to 716 million metric tonnes (1 metric tonnes=1000 kg) during 1990 to 2017 (carbon dioxide (CO_2) equivalent). The CO_2 originated due to fossil fuels' consumption contributes the most to the country's GHG emission, which accounted for about 80% of Canada's total GHG emissions in 2017. Other GHG emissions in Canada consists of 13% CH_4, 5% nitrous oxide (N_2O) and 2% trace GHGs, such as perfluorocarbons, hexafluoride, hydrofluorocarbons, nitrogen trifluoride, along with sulfur compounds [7, 8]. Methane emissions increased by 3.8 million metric tonnes from 1990 to 2017 (about 4% increase), making Canada the 12th world anthropogenic CH_4 emitter [8, 9]. Results are not available for 2018-2020 yet [10].

In Quebec, estimated and predicted amounts of total GHG during 1990, 2017, 2020 and 2030 showed emissions of 86, 78, 85 and 86 million metric tonnes (CO_2 equivalent), respectively. Despite a 10% decrease in GHG emissions from 2005 to 2017 in Quebec due to legislations for treatment and prevention, growing GHG emissions occurs due to industrial developments [8, 11]. Among GHGs, CO_2 and CH_4 contribute the most to the global warming potency (GWP) of Quebec and N_2O was reported to be the third contributor [12].

Around 60% of CH_4 in the world originates from anthropogenic sources such as landfills, coalmines, wastewater treatment plants (WWTPs) and sewer networks (SNWs), livestock, and waste gases from refineries and petrochemical complexes, which have concentrations. A variety of other gaseous compounds, such as volatile organic compounds (VOCs, e.g. benzene (C_6H_6) and styrene (C_8H_8)) and volatile inorganic compounds (VICs, e.g. hydrogen sulfide (H_2S))

accompanies CH_4. Nitrogen dioxide (NO_2), carbon monoxide (CO) and sulfur dioxide (SO_2) can be also emitted from the same sources [13-16]. One of the main anthropogenic emission sources of GHGs is wastewater, which has been found to be the 5th largest CH_4 emitter among anthropogenic sources and responsible for 9% of total CH_4 emissions worldwide [17]. Plants used for treating residential and industrial wastewaters as well as sewage system emit GHGs mostly due to the anaerobic digestion. Wastewater production in Canada was estimated about 5500 million m^3 yr^{-1} and GHG emissions originated from wastewaters in Canada was 0.85-1.2 million metric tonnes CO_2 equivalent in 1990-2017 [8]. Province of Quebec is the 2nd largest producer of wastewater in Canada with a production rate of 1281 million m^3 yr^{-1} [18]. Worldwide, CH_4 emission from WWTPs and SNWs was anticipated to grow between 2020 and 2030 by 8%. Therefore, it is a necessity to target wastewater as an important source of CH_4 emission.

The federal regulations regarding CH_4 emissions in Canada apply generally to facilities that handle significant volumes of gas (Environment and Climate Change Canada, Canadian Environmental Protection Act Registry). For example in the upstream oil and gas sector in Canada, for facility production venting, a limit of 1,250 m^3 of CH_4 per month (15,000 m^3 per year) and for pneumatic devices, a limit of 0.17 m^3 of CH_4 per hour are considered. Quebec regulation also applies for sludge treatments. There is a «green tax» of $19.50 (increased with inflation annually) for each ton of sludge that is incinerated in WWTPs (Canadian Legislative Framework, Canadian Council of Ministers of the Environment, 2010).

Physicochemical technologies such as incineration and catalytic treatments are not feasible in case of low CH_4 concentration (<5% v/v). Biotechnological processes such as biofiltration could be considered as a promising technique for CH_4 abatement. Biofiltration of CH_4 in a biofilter is based on the bio-oxidation of CH_4 by means of biodegrading microorganisms (methanotrophs). In this bioreaction, CH_4 is biotransformed to biomass, water (H_2O), CO_2 and salts. It is important to mention that CO_2 has a GWP of 25 times less than CH_4 [9]. Feasibility and facility to install and run a biofilter along with less harmful byproducts during biodegrading pollutants led to feasibility of this bioprocess.

Mass transfer of CH_4 from gas to liquid phase (biofilm phase) and biodegradation of CH_4 in the biofilm phase by microorganisms are the two main phenomena for the biofiltration of gaseous pollutants [156]. Methanotrophs are able to consume CH_4 as a sole energy source. Several

intracellular steps during CH_4 consumption happen. The first step is the oxidation of CH_4 to methanol (CH_3OH) catalyzed by the enzyme CH_4 monooxygenase (MMO). The second step is the oxidation of CH_3OH to formaldehyde (HCHO) catalyzed by the enzyme CH_3OH dehydrogenase (MDH). Afterwards, HCHO acts as a substrate in two possible pathways: First, transform of HCHO to formate (HCOOH) and then to CO_2 and second, various assimilatory pathways leading to the synthesis of biomass [95]. Methanotrophs are classified as type I, type II, and type X based on their cell morphology, assimilatory pathway, growth temperature, nitrogen fixation, and membrane arrangement. Type I assimilate HCHO by the ribulose monophosphate pathway. Type II use the serine pathway to assimilate HCHO. Type X combine the properties of types I and II with HCHO assimilation via the ribulose monophosphate and the serine pathway [149].

Methanotrophs need nutrients for biodegrading pollutants. Lack of nutrients can have a negative effect on biofilter's performance. Nutrients are usually provided from organic packing materials or by adding nutrients, as a nutrient solution (NS), in case of using inorganic packing materials. Addition of a certain amount of nutrients does not necessarily benefit a biofilter. Lower or higher amount of nutrients injected to the biofilter both could be harmful for microorganisms. Thus, investigating on an optimized composition for a specific case would be rewarding. Impacts of NS composition and addition strategies vary depending on microbial communities, packing materials, type and inlet concentrations of pollutants, etc. In an ideal case, the packing material is able to provide the supplementary nutrients for the biofilter (like organic packings). Any supplementary nutrient addition will impose an increase in cost, especially at full-scale applications. However, most of organic packing materials are confronted with excess pressure drop, which is a serious problem for on-site applications. Few studies have been carried out to see the impacts of NS addition in CH_4 biofilters packed with inorganic supports by means of adding fresh NS [19, 20]. Utilizing fresh NS every day causes higher cost for biofilter operation. In addition, the NS effluent, drained from bottom of biofilters, contains excess nutrients and biomass. Thus, it is considered as wastewater and has to be treated. It is not in interest to treat waste gases in the biofilter and in the same time produce a considerable amount of wastewater. There is a need for research to find a cleaner and more cost effective way of NS addition. Recycling NS could be an innovative and practical approach to decrease the nutrient

consumption. Although, biofilter must be examined to make sure about a promising performance with the new NS addition strategy.

Accompanying of non-methane organic compounds (NMOCs) such as alkanes, alkenes, chlorinated compounds, aromatics, etc. (concentrations of up to 0.1% v/v (1000 ppmv)) with CH_4 in polluted air injected to biofilters is one of the other important challenges in CH_4 biofiltration [21-23]. Interactions between CH_4 and NMOCs during bio-oxidation in the biofilter might happen and biodegradation of one component might stop the biodegradation of the other component. In this case, a decline in biofilter's performance could occur. Styrene, as one of the NMOCs, was shown to be a dangerous compound while released to the atmosphere, due to the carcinogenic effects on human body [24]. Waste gases which are emitted from WWTPs and SNWs could contain CH_4 (<5% v/v) and C_8H_8 (<0.1% v/v), simultaneously [17, 22, 25, 26]. Few researchers reported C_8H_8 elimination in biofilters [27-30], while, to our knowledge, no investigation on the simultaneous biofiltration of C_8H_8 and CH_4 has been done. Therefore, the potential for NMOCs such as C_8H_8 to affect the performance of a CH_4 biofilter is a challenging issue and needs more attention.

Investigating biofiltration of a binary system (CH_4+C_8H_8) and recycling NS in the biofilter are the novelties of the current study. To the author's best knowledge, no other study discussed the effect of recycling nutrient solution in CH_4 biofilters in order to reduce leachate (wastewater) production. In addition, presence of a NMOC like C_8H_8 in a CH_4 biofilter and the associated restrictions that might occur in terms of CH_4 RE, C_8H_8 RE and the total EC have never been investigated. Moreover, no critical review on the emission and bioelimination of CH_4 from WWTPs has been carried out before.

The hypotheses of this work are:

- Wastewater treatment plants and sewer networks are emitting CH_4 and CO_2.
- Biofiltration is a promising bioprocess to eliminate CH_4 as a greenhouse gas emitting from wastewater treatment plants.
- Biofilter performance is influenced by nutrient solution addition strategies.
- Recycling nutrient solution is a reasonable strategy in order to decrease the utilization of fresh nutrient solution and the production of leachate.
- Biofiltration is a promising method to eliminate styrene as a VOC presents in waste gases.

- Biofilters are able to eliminate CH_4 and styrene as pollutants in mixed gaseous emissions, simultaneously.
- Biofilter is working efficiently for at least one year to remove pollutants.
- Methane elimination in biofilters is intensively restricted by mass transfer from gas phase to liquid phase.
- The toxicity risk for biocatalysts and side-products of styrene biodegradation have negative effects on CH_4 biofilters.
- Clogging and pressure drop depend on packings.

The general objective of this study is to investigate the performance of CH_4 biofilter while recycling NS and examine the CH_4 biofilters' performance in the presence of C_8H_8. This study is carried out under specific objectives.

- The first specific objective will be to review CH_4 emissions from industrial wastewater, municipal wastewater and sewage systems. The techniques available for biodegradation of low CH_4 concentrations (<5% v/v) and bioreactor configurations will be studied for treatment of polluted air, which focus on CH_4 bioelimination systems.
- The second specific objective will be to evaluate the performance of a CH_4 biofilter by means of NS addition modification. Recycling a limited amount of NS, as a new strategy, will be investigated at different CH_4 inlet concentrations.
- The third specific objective will be to examine the performance of biofilters packed with inorganic supports for treating CH_4 and C_8H_8. The inhibitory effect that might occur because of C_8H_8 presence during CH_4 biodegradation will be studied. Methane biofilter will be studied solely and in presence of different concentrations of C_8H_8. Effects of CH_4 and C_8H_8 inlet concentrations on individual and total RE and EC will be evaluated. In addition, the effect of C_8H_8 on the macrokinetic parameters of CH_4 biofiltration will be studied based on the Michaelis-Menten model.

The current thesis includes five chapters containing a review paper and two experimental papers. Chapter 1 is the introduction. An overall view about the topic along with the problematic and objectives of the project are presented in this chapter.

Chapter 2 presents a comprehensive literature review on the emission of CH_4 from WWTPs (municipal and industrial) and SNWs (rising main and gravity). Biotechnological approaches for mitigation of low CH_4 concentrations (<5% v/v) such as biofilters, biotrickling filters,

bioscrubbers and two-liquid phase bioreactors are described. In addition, main parameters affecting biofilters' performance such as residence time, operating conditions, nutrient content, packing materials, mass transfer and kinetic limitations are discussed.

Chapter 3 presents different NS addition strategies for CH_4 removal in a lab-scale biofilter. Different situations such as recycling NS, adding a certain amount of fresh NS, adding NS in portions and absence of NS are studied. Besides, the effect of increasing CH_4 IL is studied at different NS addition situations. In order to study the nutrients' consumption in leachate, concentrations of nitrate (NO_3^-), sulfate (SO_4^{2-}) and phosphate (PO_4^{3-}) are measured and reported.

Chapter 4 is dedicated to CH_4 and C_8H_8 biofiltration as a mixture. Efficiencies of four CH_4 biofilters in the absence and presence of C_8H_8 are investigated. The sensitivity of the biofilters to CH_4 concentration variations and C_8H_8 concentration variations are discussed. In order to analyze the biofilters' behavior according to CH_4 and C_8H_8 inlet and outlet concentrations, a macrokinetic study based on the Michaelis-Menten model is carried out.

Chapter 5 is the conclusion of the thesis, which contains the general findings of the project and future outlook.

CHAPTER 2 Literature review

Avant propos:

L'article "Bioelimination of methane emissions from wastewater treatment plants: a review" a été soumis dans le journal "Critical Reviews in Biotechnology", juillet 2020.

Titre: Bioélimination des émissions de méthane dans les stations d'épuration des eaux usées: une revue de littérature

Title: Bioelimination of methane emissions from wastewater treatment plants: a review

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Contribution to the document: This review paper presents a literature review on the emission of CH_4 from wastewater sources and the techniques available for removal of low CH_4 concentrations encountered in this area. This review paper presents the techniques available for removal of CH_4 and other possible emissions such as VOCs, which is relevant to the main objective of the thesis.

Bioelimination of methane emissions from sewer networks and wastewater treatment plants

2.1 Résumé

Les eaux usées des maisons d'habitation et des industries sont collectées et transportées vers des stations d'épuration (STEP) via des réseaux de canalisation (SNW). Le fonctionnement des STEP entraîne des émissions directes de gaz à effet de serre (GES), tels que le méthane (CH_4) et le dioxyde de carbone (CO_2), en raison de la digestion anaérobie. Les eaux usées sont la cinquième source d'émissions anthropiques de CH_4 au monde et représentent 9% des émissions mondiales totales de CH_4. Les émissions de CH_4 des STEP devraient augmenter de 8% entre 2020 et 2030, ce qui fait des eaux usées une source croissante d'émissions de CH_4 dans le monde. Cette revue traite de la production de CH_4 à partir des STEP et des SNW ainsi que des techniques disponibles pour la biodégradation de faibles concentrations de CH_4 (< 5% v/v), habituellement présents dans ces installations. Différentes configurations de bioréacteurs utilisés pour le traitement de l'air pollué sont présentées, mettant en avant les systèmes de biofiltration du CH_4. Finalement, les principaux facteurs influençant les performances des biofiltres pour le traitement des émissions de CH_4 provenant des STEP sont discutés.

Mots-clés: Réchauffement climatique, Gaz à effet de serre, Gaz résiduels, Traitement biologique, Système de canalisation, Biofiltration.

2.2 Abstract

Wastewaters from residential houses and industries are collected and transported to wastewater treatment plants (WWTPs) via sewer networks (SNWs). The operation of WWTPs result in direct emissions of greenhouse gases (GHGs), such as methane (CH_4) and carbon dioxide (CO_2), due to the anaerobic digestion. Wastewater is the fifth largest source of anthropogenic CH_4 emissions in the world and represents 9% of total global CH_4 emissions. Methane emissions from WWTPs are expected to grow by 8% between 2020 and 2030, which makes wastewater a growing source of CH_4 emissions worldwide. This review initially considers the production of CH_4 from WWTPs and SNWs and the techniques available for biodegradation of low CH_4 concentrations (<5% v/v). It reviews different bioreactor configurations studied for treatment of polluted air and then focuses on CH_4 biofiltration systems. Major factors influencing biofilter's performance for treating CH_4 emissions from WWTPs are discussed.

Keywords: Global warming, Greenhouse gas, Waste gas, Biological treatment, Sewage system, Biofiltration.

2.3 Introduction

Wastewaters are the mixed liquid and solid wastes collected through sewers and delivered to WWTPs. During the biological wastewater treatment processes in WWTPs, CH_4, CO_2 and nitrous oxide (N_2O) could be produced through anaerobic digestion [17]. China, India, Indonesia and United States together account for about 50% of the world's CH_4 emissions from wastewater. In China, between 2000 and 2014, wastewater CH_4 emissions (WWMEs) increased from 1.35 to 3.4 million metric tonnes and from 2015 to 2020 was estimated to increase from 3.9 to 5.2 million metric tonnes [31].

Worldwide WWMEs were expected to grow by approximately 20% since 2005 and reach 27 million metric tonnes in 2020. From 2020 to 2030, WWMEs are expected to increase by 8% [9]. According to Intergovernmental Panel on Climate Change (IPCC), total WWME was 75 million metric tonnes between 2000 and 2009 [32]. Emissions Database for Global Atmospheric Research (EDGAR) estimated the WWME in 2010 around 32 million metric tonnes [31]. However, the United States Environmental Protection Agency (EPA) reported the amount of 24 million metric tonnes for 2010 worldwide [33]. Wastewater is one of the growing sources of anthropogenic CH_4 emissions [34].

Worldwide wastewater is the sixth largest contributor to N_2O emissions, accounting for approximately 3% of N_2O emissions from all sources. Nitrous oxide has detrimental GHG effects, 300 times more than CO_2. Total N_2O emissions from wastewater were expected to grow by 13% between 2005 and 2020 worldwide [17].

Amount of emissions varies based on the type of influent (municipal vs. industrial wastewater), volume of influent and the specific treatment processes used [35]. In a WWTP, CO_2 production is attributed to two main factors: biological treatment process and electricity consumption. In the sludge line, organic carbon of wastewater is converted mainly to CO_2 and CH_4 during anaerobic digestion and finally, CH_4 is oxidized to CO_2 if biogas goes through combustion [35]. The extent of CH_4 production depends primarily on the quantity of degradable organic material in the wastewater and the temperature. With increase in temperature, the rate of CH_4 production increases. This is especially important in uncontrolled systems and in warm climates [17]. The main sources of CH_4 detected in WWTPs are the sludge line units where anaerobic digestion is being carried out: the primary sludge thickener, the centrifuge, the exhaust gas of the generation

plant, the buffer tank for the digested sludge and the storage tank for the dewatered sludge. These units contribute to around 72% of CH_4 emissions of the WWTPs while the remains are emitting from the biological reactors and can be mainly attributed to the CH_4 dissolved in the wastewater, which was not totally removed by the biological system. Produced CH_4 gas can be explosive and combustible [36-38].

Sewer network (SNW), which collects and transports wastewaters from residential houses or industries to WWTPs, also emits CH_4. Sewer network is an important component of urban water infrastructure. Methane production from SNWs accounts for 18% of the overall carbon footprint of wastewaters. The other carbon compounds contain CO_2 and VOCs. Methane emissions from SNWs mostly occurs under turbulence at structures exposed to the atmosphere, such as pumping stations [39].

In the past years, GHG emission is one of the factors that has been taken into consideration due to examine the overall performance of WWTPs. According to Environment and Climate Change Canada (Reporting Requirements of 2016, Greenhouse Gas Emissions), the category of "wastewater emissions" refers to releases that result from wastewater and WWTPs. Methane emitted from wastewater treatment processes (aerobic and anaerobic) has been reported under this category. Considering the importance of controlling and decreasing the concentration of CH_4, the main aim of this study is to investigate on methods of eliminating CH_4 emitted from WWTPs and SNWs.

2.4 Methane emissions from wastewaters

Methane as a detrimental GHG has a great contribution to warming of the earth's climate. The major source of CO_2 is derived from fossil fuel combustion, but in case of CH_4, the main source is uncontrolled anaerobic degradation of organics, from either natural or anthropogenic sources [40]. Wastewater as one of the most important anthropogenic sources of CH_4 emission originates from a variety of residential and industrial sources. Sewer network, which is used to transport wastewater, is also a primary source of CH_4 emission. Methane emitting from wastewater during transportation (SNWs) and during treatment in WWTPs is considered as a notorious gas that should be prevented or eliminated.

2.4.1 Methane emitted from municipal wastewater

In a city, many infrastructures are provided just for water supply and sanitation. Due to urban intensification, the urban water cycle is a key point that needs to be considered in order to find origins of GHG emissions. Generally, urban water cycle contains 6 main phases: 1-water supply, 2-drinking water treatment, 3-water transport and distribution, 4-water use, 5-sewerage and rainwater transport and 6-wastewater treatment [41, 42]. Carbon dioxide, CH_4 and N_2O, as well as many other gases, such as volatile organic compounds (VOCs, e.g. benzene (C_6H_6) and toluene (C_7H_8)) and volatile inorganic compounds (VICs, e.g. sulfur dioxide (SO_2) and hydrogen sulfide (H_2S)) are emitted as a result of biological processes in WWTPs [43, 44].

Methane in a WWTP could be emitted either after it enters the plant via stripping from the incoming wastewater, or after it is formed in situ at the plant. Methane, which was formed in sewer system while transporting, could be present as dissolved compound in the wastewater stream in the plant [36, 45, 46]. Bacterial decomposition of organic matter in the absence of oxygen in residential and industrial wastewaters leads to CH_4 production. Aerobic decomposition process in wastewater demands more oxygen than can be supplied by surface diffusion. If there is no mechanical aeration, anaerobic decomposition of organic matter is activated by methanogenic bacteria, which will produce CH_4 as the result [47].

In a long-term study on a municipal WWTP near Rotterdam, Netherlands, CH_4 was found to account for 13.5% of all GHG emission, even more than the CO_2 produced due to providing plant's energy (electricity) [48]. Likewise, the proportion of CH_4 in the climate footprint of a WWTP near Gothenburg, Sweden, was estimated at 31% [49, 50]. In a large municipal WWTP (270,000 $m^3_{sewage}.d^{-1}$) in Helsinki, Finland, annual CH_4 emission were reported to be around 350 metric tonnes (3.5 $g_{CH4}.m^{-3}_{sewage}$) [51]. In the US, wastewater treatment was reported to be the seventh most important source of CH_4 emission [50, 52], while on a world scale, wastewater treatment made up for 9% of the total CH_4 emission [53, 54]. Investigation on seasonal variations of GHG emissions from a WWTP in Sendai city, Japan, by Masuda *et al.* [55] showed that the main emissions are related to CO_2 from electricity consumption (plant's energy source), N_2O from the sludge incineration and CH_4 from the liquid treatment processes. The major CH_4 emission sections (descending order) were anaerobic tanks, oxic tanks, aerated chambers and sludge concentration tanks [56].

Daelman *et al.* [36] also studied a full-scale municipal WWTP, Kralingseveer, located in the municipality of Capelle aan den IJssel, near Rotterdam, the Netherlands, with sludge digestion during one year. Three quarters of the total CH_4 emission was originated from the anaerobic digestion of sludge. Regarding dissolved CH_4 in digester and storage tanks, it could be stripped during downstream processing such as dewatering of digested sludge, or remained dissolved in the reject water. Reject water with its CH_4 content was transferred to aeration tank, same as what influent stream went through. In aeration tanks, dissolved CH_4 could be either stripped during aeration, or biologically oxidized to CO_2 [36]. To avoid dissolved CH_4 goes to atmosphere, Hatamoto *et al.* [57] and Matsuura *et al*. [58] developed a biofilm reactor, while van der Ha *et al*. [59] introduced a co-culture of methanotrophic bacteria and microalgae to degrade CH_4 in the effluent of an anaerobic WWTP. Czepiel *et al*. [47] studied a small WWTP (12,500 persons) in Durham, New Hampshire, USA, with CH_4 emission of 39 $g.person^{-1}.yr^{-1}$ (0.14 $g.m^{-3}_{influent}$). The plant studied by Wang *et al*. [56] in Jinan, China, was quite a large plant (1,500,000 persons) with CH_4 emission lower than Durnham's of about 11 $g.person^{-1}.yr^{-1}$ (0.16 $g.m^{-3}_{influent}$). Data on 3 other WWTPs, monitored by the Dutch Foundation for Applied Water Research showed CH_4 emissions of 266 $g.person^{-1}.yr^{-1}$ (2.44 $g.m^{-3}_{influent}$) for Papendrecht WWTP (40,000 persons) and 140 $g.person^{-1}.yr^{-1}$ (1.56 $g.m^{-3}_{influent}$) for Kortenoord WWTP (100,000 persons). For Kralingseveer WWTP (360,000 persons), CH_4 emissions of 310 $g.person^{-1}.yr^{-1}$ (2.73 $g.m^{-3}_{influent}$) during October and 230 $g.person^{-1}.yr^{-1}$ (2.03 $g.m^{-3}_{influent}$) during February were monitored [36, 60]. The abovementioned reports, illustrate an average CH_4 emission of 1.5 $g.m^{-3}_{influent}$ from municipal WWTPs.

2.4.2 Methane emitted from industrial wastewaters

Generally, only the industry that produces wastewater with a large amount of organic matter is amenable to emit CH_4, i.e. meat and poultry industry, pulp and paper industry, fruits, vegetables and juice processing industry [61-63]. Industrial wastewaters are usually preliminarily treated inside the industries and then discharged into the SNW to integrate with domestic wastewaters for more treatments [64]. Regarding industrial wastewater, CH_4, N_2O and CO_2 are predominant GHG emissions. The food industries (like snacks factories) produce considerable amounts of lipid-rich wastes in slaughterhouses and in the processing of edible oils, dairy products and olive

oils. Wastes of fat, oil and grease contain high amount of biodegradable volatile solids ranging from 17 to 93% (w/w) [65, 66]. The composition of anaerobic digester's gases can vary with the process conditions and seasonal ambient temperatures (hot summers and freezing winters). Typical average gaseous emissions are 65±5% CH_4 (v/v), 35±5% CO_2 (v/v) and trace amounts of H_2S [67]. Digesters treating lipid wastes theoretically produce 1.4 $m^3_{biogas}.kg^{-1}_{fat}$ with CH_4 content of 70% (v/v) [68, 69]. Dairy production facilities are important industrial wastewater sources, as a large volume of water is used in all production steps and in equipment cleansing. Effluents from dairy production systems are rich in carbohydrates, proteins and fats which are major sources of wastewater pollution and CH_4 production [70, 71].

In Denmark, 80% of all industries are connected to municipal WWTPs [72]. The Danish emission in 2011 was estimated to 3,200,000 kg CH_4 and 260,000 kg N_2O [73]. A study conducted by Glaz *et al*. [12] on GHG emissions from waste stabilization ponds (WSPs) in Quebec (Canada) showed 0.23-10.5 $g_{biogas}.m^{-2}_{pond}$ CH_4 production annually. In Canada, the piggery industry is an essential part of the agricultural sector [74]. Nutrients' concentrations, like carbon and nitrogen, in swine slurry are expected to be at least 60 times more than what were estimated in municipal wastewaters [75]. Wastewaters originated from piggery industry are usually stored in anaerobic conditions and lead to GHG emissions (mostly CH_4 and N_2O). Methane concentration from piggery wastewater storages was reported to vary from 0.1 to 20 $g.m^{-3}$ (0.02 to 3.1% v/v) [74, 76].

Volatile organic compounds (VOCs) are also produced during treatment of industrial wastewaters. In addition, while transporting in SNWs, VOCs are released to atmosphere during turbulent flow and air exchange between ambient atmosphere and wastewater, depending on properties of chemicals and fluid flow characteristics [41]. There is a growing concern regarding several VOCs that could be emitted from wastewaters, especially industrial effluents. A large variety of VOCs, such as benzene (C_6H_6), styrene (C_8H_8), acetone (C_3H_6O), chloroform ($CHCl_3$), ethylbenzene (C_8H_{10}), toluene (C_7H_8), xylene (C_8H_{10}), methanol (CH_3OH) and ethanol (C_2H_5OH) as well as volatile inorganic compounds (VICs), such as H_2S, nitrogen monoxide (NO), nitrogen dioxide (NO_2) and sulfur dioxide (SO_2) are mostly found in wastewaters from refineries and petrochemical complexes and industries related to solvents, paints, varnishes, pesticides and adhesives [13-15]. Therefore, investigating on processes to eliminate GHGs and VOCs/VICs, simultaneously, should also be taken into consideration.

2.4.3 Methane emitted from sewer networks

The SNWs could be assumed as biological plug flow reactors [77], in which mostly CH_4, CO_2, N_2O and H_2S are formed by aerobic, anoxic or anaerobic processes, depending on the type of sewer (gravity or pressurized), type of constructive elements and independent variables of pipeline geometry (i.e. surface area to volume ratio) [45, 78]. In a comprehensive study by Liu *et al*. [79], CH_4 production mechanisms in sewers, production and emission modeling, measurement and effects of chemical dosing (oxygen, nitrogen, pH, etc.) on CH_4 formation in sewers were investigated. Sewer systems can be divided into two categories: first, pressure sewers (rising main sewers), which are anaerobic, and second, gravity sewers, which involves re-aeration. Regarding a sewer pipe, five major phases could be considered: 1. Suspended wastewater/biomass phase 2. Wetted sewer biofilms 3. Sediments 4. Sewer air phase 5. Biofilm on pipe surface exposed to sewer air (phases 4 and 5 are only present in gravity sewers). Microbial processes in sewers mostly occur in biofilms and sediments. Little contribution is related to suspended biomass in the water phase [39, 80]. Due to the explosive limit of CH_4, which is about 5% (v/v), uncontrolled emissions of CH_4 could end up with an explosion while exposing with air in networks' limited space [81]. Therefore, continuous formation of CH_4 in SNWs is followed by a risk in the system [46]. Guisasola *et al*. [46] reported more than 20 $g.m^{-3}$ dissolved CH_4 in rising main sewers. Gaseous CH_4 in concentrations of up to 5% v/v (50,000 ppmv) in the atmosphere around gravity sewer systems were reported [82]. Eijo-Río *et al.* [44] studied formation of CH_4, N_2O and H_2S in sewers and conducted sampling campaigns in two Spanish cities. Regarding the city Calafell, CH_4 emissions of 18.6 $kg.yr^{-1}$ during summer and 3.8 $kg.yr^{-1}$ during winter were measured (80% decrease). For the other city, Betanzos, 24.6 $kg.yr^{-1}$ during summer and 10 $kg.yr^{-1}$ during winter were reported (60% decrease), which proved that temperature is a key factor while transporting sewers in networks [44].

In rising main sewers, wetted anaerobic biofilms are present. In gravity sewers, both biofilms and sediments are in anaerobic conditions, due to the limited penetration of the oxygen present in the bulk wastewater [83]. In deeper layers, anaerobic fermentation along with sulfate reduction utilizing organic matter could occur [84]. The products of mentioned anaerobic fermentation could produce CH_4 by methanogenic archaea present in sewer biofilms [85, 86].

As shown in Table 2.1, CH_4 was produced in rising main and gravity sewers along with pumping stations (on the way to WWTPs) up to 15.1 $g.m^{-3}$, almost similar to CH_4 emissions from wastewater (e.g. 20 $g.m^{-3}$ from swine slurry) [39]. In Gold Coast, Australia, dissolved CH_4 with concentrations of 4.4 to 6.1 $g.m^{-3}$ was detected at the end of an 828-meter-long rising main SNW (average CH_4 production of 1.1 $kg.d^{-1}$). Fluid flow in the pipe was 200 $m^3.d^{-1}$ [82, 87]. Liu *et al*. [88] reported an average dissolved CH_4 of 9.1 $g.m^{-3}$, depending on hydraulic retention time (HRT) in the network. The HRT is a measure of the average length of time that sewage remains in pipes of SNW on the way to WWTP [89].

Table 2.1: Methane production measured in liquid phase

Sewer network system	Average wastewater temperature (°C)	Average HRT (h)	Daily sewage flow ($m^3.d^{-1}$)	Average dissolved CH_4 ($g.m^{-3}_{ww}$)	Ref.
Rising main	27.7	2.5	200	5.3	[82]
Rising main	22.5	2.6	707	15.3	[82]
Rising main	24.6	9.1	2840	9.1	[88]
Rising main	–	–	11,000	4.8	[90]
Gravity	33.3	27.9	–	10.1	[91]
Pumping station	23.5	–	707	1.5	[45]
Pumping station	–	–	2000	0.51	[90]

While CH_4 emission occurs in gravity sewers, following sewage discharge from an upstream rising main, remarkable part of CH_4 still remains in liquid phase and emits at downstream gravity section or downstream WWTP inlet [91]. Dissolved CH_4 concentrations monitored to be very low in pumping stations, like stations in Queensland (Australia) with concentrations of 0.5 to 1.5 $g.m^{-3}$ [88]. As shown in Table 2.2, when sewage flow from an enclosed anaerobic sewer pipe is discharged into a ventilated space, i.e. pumping station, wet-well, gravity sewer or even WWTP, a large part of dissolved CH_4 will be released to the atmosphere [39]. For example

in Perth (Australia), CH_4 was emitting with concentrations between 0.7 and 1.2% (v/v) at a sewage flow rate of 17,000 $m^3.d^{-1}$ discharged from a gravity sewer [90]. Data from several manholes receiving industrial wastewaters in Melbourne (Australia) presented CH_4 emissions of around 5% v/v [82]. An average CH_4 emission of about 0.7% v/v was reported from gravity sewers located in central Thailand [91]. Methane formation in sewer is not limited to warm countries such as Thailand and Australia. A field study during autumn, which was conducted in Boston (USA), revealed that many manholes have CH_4 concentrations even more than 5% v/v [92].

Table 2.2: Gaseous CH_4 measured in atmosphere around sewer networks

Location	Sewer network type	Daily sewage flow ($m^3.d^{-1}$)	CH_4 (% v/v) average (min–max)	Ref.
Perth, Australia	Gravity	17,000	0.9 (0.7–1.2)	[90]
Thailand	Gravity	–	0.7	[91]
Melbourne, Australia	Gravity	–	0.15–5	[82]
Perth, Australia	Rising main	11,000	2 (1.5–2.9)	[90]
USA	Rising main	1,855	0.06 (0.05–0.09)	[93]
Melbourne, Australia	Rising main	707	1 (0.25–0.45)	[82]
Gold Coast, Australia	Pumping station	2,000	0.22 (0.14–0.28)	[90]
USA	Pumping station	378.5	0.01 (0.01–0.03)	[93]

Due to special situation of SNWs, CH_4 released into the atmosphere, is not easy to treat and considered as an important challenge in large scales with an important contribution to global warming in the last decade. To our knowledge, no treatment method has been introduced for the CH_4 emitted directly in SNWs (e.g. CH_4 emissions from sewage manholes and pumping stations). All efforts have been made so far involve treating SNWs' CH_4 (gaseous and dissolved)

after sewage discharge into WWTPs. In regards to CH_4 elimination in WWTPs, at low CH_4 concentrations (i.e. from below 7 up to 33 $g.m^{-3}$), biotechnological treatments such as biofilters (BFs) are more promising and cost-effective compared to physicochemical processes (e.g. incineration and catalytic oxidation) [94, 95]. The bioprocesses for elimination of low concentration WWMEs (0.1-5% v/v) are briefly summarized hereafter.

2.5 Bioreactors for CH_4 elimination

Biotechnological processes are more promising and cost-effective at low emission concentrations compared to physicochemical processes [94, 95]. Biological techniques were initially applied at WWTPs for odor removal [96]. Same facilities with some modifications might be useful for different gaseous pollutants removal. Low concentrations of pollutants emitting from WWTPs in most cases contain carbon and hydrogen atoms, e.g. CH_4, accompanied with VOCs, e.g. C_8H_8, CH_3OH, and VICs such as H_2S. The final products of CH_4 bio-oxidation are water, CO_2, biomass and salts. Biomass not only contains carbon, hydrogen and oxygen atoms, but also nitrogen and other elements such as phosphorus and sulfur are present in the biomass sometimes [94]. Researches have been studying on development of biotreatment systems in order to eliminate the gaseous emissions from anthropogenic sources, which have the potency to be utilized for elimination of CH_4 emitting from WWTPs.
In order to evaluate bioreactor's performance, the following parameters are used:

$$\text{Inlet load (IL)} = \frac{C_{in} \times Q}{V} \quad (g.m^{-3}.h^{-1}) \qquad (1)$$

$$\text{Removal efficiency (RE)} = \frac{C_{in} - C_{out}}{C_{in}} \quad (\%) \qquad (2)$$

$$\text{Elimination capacity (EC)} = IL \times RE \quad (g.m^{-3}.h^{-1}) \qquad (3)$$

Where C_{in} and C_{out} are the pollutant inlet and outlet concentrations ($g.m^{-3}$), respectively. Q is the gas flow rate ($m^3.h^{-1}$) and V is the bioreactor volume (m^3). Empty bed residence time and temperature are shortly referred as EBRT and T, respectively.

2.5.1 Biotrickling filters

Continuous feed of a liquid phase and inert packing materials in all cases are the main features of biotrickling filters (BTFs). Regular supply of nutrients provide an efficient performance for biotrickling systems in regard to waste gas treatment [97]. In regards to treating gaseous emissions from wastewaters, Pirolli *et al*. [98] developed a simple and low maintenance field-scale BTF for desulfurization of swine wastewater (inlet biogas flow rate of 0.024-0.048 $m^3.h^{-1}$). The BTF was continuously fed with wastewater effluent from an air sparged nitrification-denitrification bioreactor (H_2S inlet concentrations of 518-1,705 $g.m^{-3}$). Maximum H_2S RE of 99.8% was achieved with a maximum EC of 1,509 $g.m^{-3}.h^{-1}$. The ECs obtained for inlet biogas flow rates of 0.024, 0.036 and 0.048 $m^3.h^{-1}$ were 718, 1013 and 438 $g.m^{-3}.h^{-1}$, respectively. A similar configuration could be utilized for removing CH_4 emitted from the WWTP. Table 2.3 represents few examples for BTF utilization in CH_4 elimination. Zhu *et al*. [99] investigated on the effects of nutrient solution (NS) addition (nitrogen and phosphorus concentration) on bio-elimination of low concentration CH_4 (0.1-1% v/v), similar to CH_4 concentrations emitting from WWTPs, in a BTF packed with ceramic pall rings (flow rate of 0.12 $m^3.h^{-1}$). By increasing inlet CH_4 from 0.1% to 1% (v/v), RE decreased from 98 to 40%.

Table 2.3: Methane removal in biotrickling filters.

Packing material	Removal efficiency		Ref.
	Inlet load ($g.m^{-3}.h^{-1}$)	RE (%)	
Polyurethane foam	160	16	[100]
Stone	67	40	[101]
Polyethylene rings	3	50	[102]

2.5.2 Bioscrubbers

When a suspended growth bioreactor (SGBR) is combined with a conventional scrubber (SC), it is called bioscrubber (BSC). These two units work separately. An important advantage of BSCs is the capability to work at high gas loads up to 4000 $m^3.m^{-2}.h^{-1}$ (corresponding loads in

biofilters (BFs) do not exceed 500 $m^3.m^{-2}.h^{-1}$) [96]. When polluted air is injected, the SC works as an absorption tower. The effluent air from SC is released to the atmosphere and contaminated water goes to the SGBR. Microorganisms (MOs) present in the aqueous phase in SGBR (suspended biomass) undertake the biodegradation of pollutants in the bioreactor [103-105]. Instead of injecting polluted air to a SC and then treating the polluted aqueous phase in a SGBR, it is also possible to inject polluted air to a stirred tank bioreactor directly. For instance, in a WWTP, an activated sludge reactor (already available on-site) could be used. It will be a reasonable approach for industrial plants that need to treat both wastewater and waste gas (including CH_4), simultaneously [106].

2.5.3 Two-liquid phase bioreactors

Methane removal in bioreactors, such as BTFs is influenced by several parameters, such as variations in operating conditions and limitations in mass transfer due to poor solubility of CH_4 in the aqueous phase (0.00126 $mol.kg^{-1} \approx 20.21\ g.m^{-3}$ at 30°C and 1 atm) [107]. Poor solubility of CH_4 leads to a need for high EBRTs, which subsequently requires either a large size of the bioreactor or a low gas flow rate, which is not cost effective. For instance, the value of EBRTs in the majority of BFs are less than 1 minute for hydrophilic components (i.e. CH_3OH). However, for hydrophobic pollutants, i.e. CH_4, it needs to be at least 2 min, up to 30 min sometimes [108, 109]. A second liquid phase (SLP) in bioreactors might impose a driving force that allows more pollutant to be transferred from gas phase to the liquid phase, desirable for poorly water soluble compounds. In addition, since MOs are mostly in the first liquid phase (FLP), which is mostly water, they are not exposed to inhibitory pollutants accumulating in SLP [94]. The SLP should involve properties such as: inexpensive, non-biodegradable, non-toxic to MOs, low vapor pressure, immiscible with FLP, density different from the density of FLP [110]. It is not recommended to use viscous solvents at full-scale due to pumping problems [111]. Silicone oil and hexadecane were reported as non-biodegradable and non-toxic solvents, which met important features of SLPs [112-115]. Table 2.4 illustrates few examples of two-liquid phase stirred tank bioreactors in terms of EC and RE. Water was used as FLP in all cases.

Table 2.4: Air treatment in two-liquid phase stirred tank bioreactor

Pollutant	Second liquid phase (SLP)	SLP/FLP (v/v %)	IL ($g.m^{-3}.h^{-1}$)	EC ($g.m^{-3}.h^{-1}$)	RE (%)	Ref.
Benzene	hexadecane	33	140	133	95	[116]
Hexane	Silicone oil	10	182	140	77	[112]
Hexane	Silicone oil	10	180	120	67	[117]
Toluene	hexadecane	33	748	733	98	[118]

The ratio of SLP to FLP should not exceed 30% (v/v) at full-scale applications. However, ratios between 5 and 50% (v/v) were reported in laboratory-scale bioreactors. When SLP/FLP goes higher than 40%, large size SLP drops are formed, which is not desirable in terms of mass transfer surface area [111, 119]. In case of using two-liquid technique in a BTF for eliminating CH_4, SLP/FLP in ranges of 0-25% (v/v) were investigated at lab-scale. Performance of two-liquid phase BTFs (water as FLP and silicon oil as SLP) for CH_4 removal are shown in Table 2.5. Rocha-Rios *et al*. [100] obtained higher CH_4 EC of 60 $g.m^{-3}.h^{-1}$ (IL of 130 $g.m^{-3}.h^{-1}$) in a BTF with SLP/FLP of 10% (v/v) compared to an EC of 25 $g.m^{-3}.h^{-1}$ (IL of 160 $g.m^{-3}.h^{-1}$) in a BTF without SLP. Lebrero *et al*. [120] obtained an EC of 45 $g.m^{-3}.h^{-1}$ at an IL of 250 $g.m^{-3}.h^{-1}$ (EBRT of 4 min) in a CH_4 BTF (SLP/FLP of 25% v/v). The results were in the range of the studies conducted by Avalos Ramirez *et al*. [101] in CH_4 BTFs (EBRT of 4 min). The improvement of the CH_4 REs and ECs in two liquid phase BTFs could be attributed to absorption properties of SLP (silicone oil) for CH_4, which provided a high rate of CH_4 mass transfer from gas phase to FLP (water) [121].

Table 2.5: Methane treatment in biotrickling filters with silicon oil as SLP and water as FLP.

IL ($g.m^{-3}.h^{-1}$)	SLP/FLP (v/v %)	EC ($g.m^{-3}.h^{-1}$)	RE (%)	Ref.
160	-	25	16	[100]
130	10	60	46	[100]
250	25	45	18	[120]

2.5.4 Biofilters

Biofilters (BFs) are referred to packed plug flow bioreactors (down flow or upflow) in which MOs on the packing materials act as catalysts and transform the pollutants in contaminated air to CO_2, biomass, water and salts [25, 94, 96, 122]. Production of CO_2 in this case may seem as a disadvantage, but considering the 25 times greater GHG impact of CH_4 compare to CO_2, it makes biofiltration a reasonable process. It means that even 50% conversion of CH_4 to CO_2 leads to a remarkable reduction in GHG potential [9, 95]. Like BSCs and BTFs, no hazardous pollutants (e.g. NO_2, SO_2 and CO) are present in the gas leaving from top of the BF column and BFs work at ambient temperature and pressure [95]. Organic packing materials, which were widely used for odor removal at WWTPs, could also be used in CH_4 BFs, such as soil, compost and peat [94, 103]. Conventional BFs due to the absence of continuous NS addition (unlike BTFs), possibility of low effluent drain from the system (less leachate) and low cost, could be a promising approach for treating CH_4 emitting from WWTPs. Since BFs could tolerate variations in ILs and shock loads and are easy to install and easily movable, they might be a potential approach to apply in WWTPs in order to treat CH_4 emitting from wastewaters [95, 123-126]. Examples of CH_4 biofiltration in different operating conditions are shown in Table 2.6. There is a need for further studies to determine optimum ranges for controlling and maintaining BFs in different situations. Researches focusing on biofiltration of gases containing CH_4, which are being emitted from SNWs and WWTPs, have still remained limited.

Table 2.6: Performance of biofiltration process in CH_4 removal for air treatment

Packing material	Operating conditions	Performance	Ref.
Gravel	Concentration=0.3% (v/v) EBRT = 6 min IL = 30 $g.m^{-3}.h^{-1}$ NS: 1.5 $L.d^{-1}$	EC = 16 $g.m^{-3}.h^{-1}$ RE = 54%	[127]

Gravel	Concentration=0.025-0.43% (v/v) EBRT = 4.2 min IL = 28 $g.m^{-3}.h^{-1}$ NS: 1.6 $L.d^{-1}$	EC = 12.3 $g.m^{-3}.h^{-1}$ RE = 43%	[128]
Sponge-based	IL = 20 $g.m^{-3}.h^{-1}$ EBRT=7.4 min T=19-36 ºC V = 8 L NS: non added	EC = 3 $g.m^{-3}.h^{-1}$ RE = 15%	[129]
Blast furnaces slag		EC = 4 $g.m^{-3}.h^{-1}$ RE = 20%	
Expanded vermiculite		EC = 6 $g.m^{-3}.h^{-1}$ RE = 30%	
Compost and sand biocover	Concentration=50% (v/v) CH_4 + 50% (v/v) CO_2 IL = 12 $g.m^{-2}.h^{-1}$	EC = 7–12 $g.m^{-2}.d^{-1}$	[130]
Mixed inorganic packings	IL=19±9.5 g m^{-3} h^{-1} Multi-layer packing: topsoil (0.1 m)+sand (0.02 m)+gravel (0.02 m)+clay (0.67 m)+gravel (0.1–0.3 m)	RE = 62% (annual basis)	[131]
Recycling paper pellets biocover	Concentration=30% (v/v) CH_4 + 70% CO_2 (v/v) IL = 4.4 $g.m^{-2}.h^{-1}$	EC = 2 $g.m^{-2}.h^{-1}$	[132]
Wood chips biocover	Concentration=30% (v/v) CH_4 + 70% (v/v) CO_2 IL = 20.2 $g.m^{-2}.h^{-1}$	EC = 19.8 $g.m^{-2}.h^{-1}$	[132]
Compost of leaves biocover	IL = 21 $g.m^{-2}.h^{-1}$	EC = 14–17 $g.m^{-2}.h^{-1}$	[133, 134]
Inorganic packing (stone-based)	IL = 80 $g.m^{-3}.h^{-1}$ EBRT=3.4 min NS: 0.6-1.8 L d^{-1} T = 30 °C	EC = 25 $g.m^{-3}.h^{-1}$ RE = 31%	[135]

Inorganic packing (stone-based)	IL = 80 $g.m^{-3}.h^{-1}$ EBRT=3.4 min NS: 0.6-1.8 L d^{-1} T = 43 °C	EC = 20 $g.m^{-3}.h^{-1}$ RE = 25%	[135]
Inorganic material	Concentration=0.7–0.75% v/v	EC = 700 $g.m^{-2}.d^{-1}$	[125]
Coal	IL = 17 $g.m^{-3}.h^{-1}$	RE = 30%	[136]
Mixture of wood chips, perlite and compost	IL = 17.5 $g.m^{-3}.h^{-1}$ EBRT = 4.4 min	RE = 62% EC = 11 $g.m^{-3}.h^{-1}$	[137]
Inorganic packing	Concentration=0.1-0.4% v/v IL = 87 $g.m^{-3}.h^{-1}$	RE ≥ 75% EC = 45 $g.m^{-3}.h^{-1}$	[123]
Compost	Concentration=2% (v/v) EBRT = 20 min	EC = 37 $g.m^{-3}.h^{-1}$ RE = 90%	[138]
Compost	IL = 100 $g.m^{-3}.h^{-1}$ EBRT = 23 min NS: non added	RE = 70%	[139]
Biochar/lava rock/compost	IL = 36 $g.m^{-3}.h^{-1}$ EBRT = 83 min NS: non added	RE = 100%	[140]

A report issued by the Canadian Pork Council indicated RE of 50-60% (EC of 16-20 $g.m^{-3}.h^{-1}$) for bioelimination of CH_4 in BFs (EBRT of 10 min) packed with four different organic materials (without inoculation). Mixtures of compost, wood chips, soil and peat were used as packing materials. The CH_4 (0.2-3.5% v/v) was being emitted from a 3,800 m^3 wastewater storage (swine slurry) at an average IL of 30 $g.m^{-3}.h^{-1}$ [141]. Bioelimination of CH_4 originated from wastewater reservoir (6 m^3 pilot-scale slurry) by means of BFs was also done by Mesle and van der Werf [76]. A BF packed with compost/perlite and an EBRT ranging between 1 and 80 min was utilized for CH_4 IL of 1 to 25 $g.m^{-3}.h^{-1}$. The inoculation of the BF was carried out with activated sludge from WWTP. At concentration of 0.85% v/v, CH_4 RE of 85% was obtained.

2.5.5 Hybrid systems

Air treatment in hybrid systems involves two or more bioreactors (either same or different bioreactors) in order to achieve a complete or higher removal of a target pollutant, or a mixture of pollutants, simultaneously [94]. Rene *et al*. [142] used a combination of a BTF and a BF to treat a mixture of H_2S (IL of 20 $g.m^{-3}.h^{-1}$), CH_3OH (IL of 200 $g.m^{-3}.h^{-1}$) and pinene ($C_{10}H_{16}$ IL of 50 $g.m^{-3}.h^{-1}$). The complex mixture of $H_2S/CH_3OH/C_{10}H_{16}$ is originated in WWTPs or wood industries, like pulp and paper industry. In BTF, RE of 98% for both H_2S and CH_3OH and 40% for $C_{10}H_{16}$ were achieved. The BF located in the second stage, in series after the BTF, resulted in $C_{10}H_{16}$ RE of 90%. In a WWTP, combination of two BFs in series for sulfur (target pollutant) removal from waste gas mixture (H_2S and VOCs) ended up with 100% H_2S RE. The hybrid system included a low pH inorganic BF (because sulfur biodegradation results in biofiltering bed acidification) followed by a neutral pH organic BF (because pH for VOCs' biodegrading bacteria is almost neutral) [143-146]. Wu *et al*. [147] used two BFs in series for elimination of xylene (C_8H_{10}), which is commonly emitted from WWTPs and other industries such as printing and coating facilities, foundries, chemical industries, electronics and paint manufacturing. An RE of 95% were achieved at C_8H_{10} IL of 85 $g.m^{-3}.h^{-1}$. Spigno *et al*. [148] also used two BFs to eliminate hexane (C_6H_{14} IL of 300 $g.m^{-3}.h^{-1}$). In the second BF, RE of 70% was observed, while C_6H_{14} RE of 50% was obtained in the first BF. Lower RE in the first BF was probably due to the higher C_6H_{14} IL. These type of hybrid systems in series could be useful for reluctant compounds like CH_4. However, to our best knowledge, there is no study on this matter in the literature.

2.6 Parameters affecting CH_4 biofiltration

Promising performance at ambient temperature and atmospheric pressure, possibility of using organic and inorganic packing materials already used in WWTPs, low effluent drain, low capital and operating costs, tolerance to ILs variations and shock loads, facility in installation and movement made biofiltration a potential approach to bioeliminate WWMEs. Key factors, such as temperature, moisture content, pH, nutrient content, EBRT, CH_4 concentration and IL, effect of trace gas components, type of packing materials, NS composition and addition strategies are

necessary to be discussed. Understanding the impacts of each factor helps researchers and technology owners to develop the whole treatment system, especially when it is utilized in full-scale and for a particular situation such as WWTPs.

2.6.1 Inoculation and acclimation period

Methanotrophic bacteria (MB) is the specific MO that biodegrade CH_4, which is aerobic and present in nature in all sorts of environments, such as wetlands, soil and wastewater [149]. The MBs first oxidize CH_4 to CH_3OH. Then, CH_3OH is transformed to formaldehyde (CH_2O) and finally, CH_2O is either oxidized to CO_2 or used for synthesis of biomass [95]. In a BF, in first days of operation, when MBs are exposed to CH_4, there will be an acclimation period and CH_4 RE is normally less than 10%. After acclimation period, when MBs are grown and activated, CH_4 RE increases to a maximum RE, which could be considered as the pseudo steady state [150, 151]. Duration of acclimation period depends on operating conditions, especially CH_4 IL. All MBs do not grow within the same range of CH_4 concentrations, therefore, choosing inoculation condition is important [133, 152]. Inoculating the packings for few times during start-up might be useful to achieve the maximum RE in shorter acclimation period [122]. In order to reach a pseudo steady state in a CH_4 BF, a period of about 20 days for CH_4 concentration range of 0.1-1% (v/v) is required [151]. A common procedure for inoculating organic packing materials is to pass a certain concentration of CH_4 through the bed for a long time [153]. A prolonged exposure of MOs and CH_4 leads to activation of MBs in the filter bed [122]. The higher CH_4 concentration, the more rapid growth of MBs will occur and eventually, the more rapid increase in bio-oxidation rate will be obtained [150]. Biofilters containing inorganic packing materials usually need inoculation with an enriched liquid sample, i.e. the leachate from an active BF. In case of using BFs for CH_4 removal in WWTPs, the wastewater itself could be used as the inoculum [123].

2.6.2 Residence Time

Relatively long EBRT is known to be one of the requirements in order to achieve high CH_4 RE in biofiltration [95]. Performance of the BF is influenced by the CH_4 diffusion from gas phase

to the liquid phase, which restricts gas absorption in the biofilm and hinders biodegradation. Methane has a low solubility in water (20.21 $g.m^{-3}$ and Henry's constants of 30 at 293 K and 1 atm) with a diffusion coefficient of 1.49×10^{-9} $m^2.s^{-1}$ at 298 K [107]. Methane should be dissolved in biofilm in order to be biologically available for MBs to degrade. This requires an appropriate contact time [95]. Nikiema and Heitz [154] reported CH_4 RE of 30 to 90% for an EBRT of 6 min (CH_4 concentration of 0.13-1.2% v/v). In a study carried out by Sly [155], at an inlet CH_4 concentration of 1% (v/v), CH_4 RE of 20 and 90% were achieved for EBRT of 5 min and 20 min, respectively. In regards to evaluating the effect of gas flow rate (0.06-0.3 $m^3.h^{-1}$) on CH_4 biofiltration (inlet concentration of 1.5 $g.m^{-3}$), when EBRT decreased from 17 to 3 min, RE declined from 100 to 40%. For CH_4 BFs, EBRT of longer than 4 min was recommended, while it is less than 1 min for VOCs. Longer EBRT means more capital cost, due to increase in BF size, which is considered as a restriction for CH_4 BFs. Hybrid systems or using a SLP might allow reaching high RE with low EBRT. Although, no study is available on optimizing of CH_4 BFs with SLP or in combination with another bioreactor (hybrid), when compared to CH_4 BF alone with water as the only liquid phase.

2.6.3 Mass transfer and kinetic limits

Both CH_4 and VOCs are being emitted from WWTPs. Mass transfer limitations and kinetic restrictions are important challenges for CH_4 treatment in a BF. It becomes even more challenging while confronting with a mixture of pollutants. Mass transfer limited pollutants involve gaseous alkanes such as CH_4 emitting from WWTPs. Absence of mass transfer limited pollutants in biofilm leads to a decrease in BF's RE [103, 121, 156]. Regarding operating parameters' impacts on mass transfer limited compounds and kinetic limited compounds, a conflict of effects could be realized [156]. It means that for simultaneous biofiltration of mass transfer limited compounds and kinetic limited compounds, it is required to find optimum operating conditions that suits both. To overcome mass transfer and kinetic limitations, in addition to optimizing operating parameters, utilization of developed configurations of BF systems such as two liquid phase BFs [157, 158], two-stage systems [142] and hybrid ones and a modification in gas injection strategies might also help. For instance, for kinetic limited compounds, split feeding of inlet gas was suggested in order to increase RE [159, 160].

Regarding mass transfer limited compounds, Estrada *et al*. [161] used gas-recycling strategy in a BTF to overcome the limits. Total CH_4 IL of 230 $g.m^{-3}.h^{-1}$ with an EBRT of 4 min and gas flow rate of 1.1 $m^3.h^{-1}$ resulted in a two-fold increase in CH_4 EC (from 15 to 30 $g.m^{-3}.h^{-1}$). The same strategy might be useful in CH_4 BFs.

2.6.4 Operating Conditions

Methane inlet loads: CH_4 itself is considered as the primary carbon source, which provides a portion of energy required for MBs to stay active in biodegradation process. Methane removal in the BF correlates with CH_4 inlet concentration [155]. Girard *et al*. [128] showed by increasing inlet CH_4 concentration from 0.025 to 0.430% (v/v) with an EBRT of 4 min, CH_4 EC increased from 2.5 to 12 $g.m^{-3}.h^{-1}$. The CH_4 concentrations were chosen based on similar situation in CH_4 emissions from wastewater of piggery industries. Dependency of CH_4 biofiltration performance to CH_4 concentration is clearer when confronted with fluctuating ILs and shock loads. An investigation by Ferdowsi *et al*. [123] on BF's performance under dynamic loading patterns revealed that sudden variations of ILs from 13 to 65 $g.m^{-3}.h^{-1}$ (inlet CH_4 concentration was increased from 0.2 to 1% v/v) resulted in a sudden increase of EC from 9 to 43 $g.m^{-3}.h^{-1}$ with no significant change in CH_4 RE. Nikiema *et al.* [162] showed that gas flow rate influence on CH_4 RE was greater than CH_4 concentration. Increasing gas flow rate from 0.06 to 0.18 $m^3.h^{-1}$ (a 3-fold increase) reduced the RE by 40%, while tripling CH_4 concentration (from 0.25 to 0.75% v/v) led to a RE decline of only 7%. Biofilters are recommended for CH_4 treatment with flow rates exceeding 100,000 $m^3.h^{-1}$ if concentration is below 5 $g.m^{-3}$ [94].

Temperature: There are few reports illustrating a temperature gradient in BFs due to bio-oxidation reaction [20, 163]. The temperature gradient throughout the bed from bottom to the top of an upflow CH_4 BF, which is usually neglected in investigations, depends on gas flow rate, type of bed filter material and BF performance (RE) [95, 125, 153]. Optimal temperature for CH_4 biodegradation in a BF was reported to be 24 to 36 °C [150, 163-166]. Working beyond this range might end up with a decrease in CH_4 BFs' performance [135, 164, 167, 168]. Performance of MOs might drop by more than 50% if the temperature is decreased from 30 to 20 ºC [169]. In case of using CH_4 BFs in WWTPs, RE could be affected by seasonal temperature variations, as had been shown by Dumont *et al*. [170, 171] in long-term experiments during

summer and autumn for piggery air treatment. During winter, temperature might fall lower than that MB could tolerate. Lisovitskaya *et al*. [172] analyzed CH_4 biodegradation under climatic conditions of Moscow (landfill) in organic packed BFs with CH_4 inlet concentration of 2.5% (v/v). The CH_4 RE of 53% was achieved at CH_4 inlet concentration of 16.5 $g.m^{-3}$. In case of temperature below 10 °C, the microbial activity could be maintained by controlling parameters such as bed porosity, moisture content and O_2 supply [25, 173, 174]. During summer (>36ºC), activity of some MBs could be stimulated, which might lead to a decline in CH_4 RE. A decline in EC was shown by Ménard *et al*. [135] for temperatures higher than 34°C when biofiltering 0.7% v/v CH_4 (gas flow rate of 0.25 $m^3.h^{-1}$). The ECs were 23, 30 and 18 $g.m^{-3}.h^{-1}$ at 24, 34 and 43 ºC, respectively. In addition, temperatures more than 45 ºC had been shown to inhibit CH_4 bio-oxidation [166, 175]. These changes in BFs' performance originates from the type of MBs responsible for CH_4 biodegradation. For example, *Methylocystis parvus is a* mesophilic type of MB and the optimal temperature for its growth lies in two ranges of 23-25°C and 31-34°C [135, 153, 176]. Investigating on pilot-scale or full-scale BFs has to be followed by seasonal studies to reveal the effect of temperature on the performance.

Bed moisture: Another critical variable in BF operation is moisture content of the filter bed. Low moisture levels (relative humidity of 16%) even for a short period of process leads to bed drying and RE reduction [169, 177]. The moisture content of BF is mainly related to the gas flow rate and packing material [167]. On the other hand, high bed moisture levels (flooding with water) could also reduce RE by preventing the mass transfer of CH_4 and O_2 to biofilm [178, 179]. In this case, water channeling could happen, which might end up with bypassing the biofilm. Water content is important in biofiltration process because it is directly related to the ability of dissolving and mobilizing CH_4. Rate of MOs' metabolic activity decreases in a low moisture medium. High rates of methanotrophic reactions occur at water content of 70-90% (relative humidity) [169, 180-184]. However, Reay *et al*. [185] reported an optimum moisture content of 30–60% (w/w) to support microbial growth in the packing material for CH_4 biodegradation [180, 181]. Few models for assessment of appropriate moisture in bed media in BFs are present in the literature. Mancebo *et al*. [186] presented results from an investigation which was based on Peleg model [187] for granular materials used as packings in BFs. Previous studies undertaken by Mancebo *et al*. [188] showed that there was a good agreement between experimental determined water content and the values predicted by Peleg model [187].

pH: Another factor which plays an important role in CH_4 bio-oxidizing reaction is the pH of filter bed. According to Hanson and Hanson [149], MBs are able to tolerate pH values ranging from 5.5 to 8.5, while Chakravorty and Forrester [189] reported a range of 5 to 7.5 as the optimum pH for CH_4 BFs. Hettiaratchi and Stein [133] found a pH of about 7 (neutral) as the best value for CH_4 biofiltration. pH in organic packing materials could stay within the optimum range, while inorganic packing materials may need adjustments in pH of the filter bed, by means of i.e. a buffer or continuous wash out [95]. To reach an optimum performance in soil-based CH_4 BFs, pH ranging between 6.7 and 8.1 was reported as optimum pH condition, while for peat, it was reported between 5 and 6.5 [150, 168]. In a study carried out to eliminate BTEX (benzene, toluene, ethyl-benzene and xylene isomers), biodegradation reaction was inhibited in acidic media (pH<7.5). Total RE was more than 80% when pH was between 7.5 and 8 [190, 191]. Lakhouit *et al*. [192] with the goal of emission reduction from a landfill (Saint-Nicéphore, Quebec, Canada) showed that BTEX RE was 67-100% when pH value of the media was 7.2 (almost neutral). If fungi are dominant, the optimal pH range will be around 5.5 and fungi might even remain active at pH values below 4 [193, 194].

2.6.5 Nutrient Content

Microorganisms (MOs) such as methanotrophic bacteria (MB), use organic carbon as energy source [94]. Therefore, CH_4 is the primary source of energy for MB to stay alive and active. However, MBs need other nutrients to survive. In a filter bed with not enough nutrients, MB will not be able to grow and may begin to die. Providing all sources of energy required for MBs is essential for CH_4 biofiltration. Nutrients such as carbon (C), nitrogen (N), phosphorus (P), copper (Cu) and potassium (K) are essential for MBs [19, 195]. Sulfur (S), magnesium (Mg), calcium (Ca), sodium (Na) and iron (Fe) are other nutrients that must be involved in NS [153]. These additional nutrients might already exist in the filter bed (if organic packing materials are used) or could be added by synthesis NS. Nikiema [162] studied the effect of NS in an inorganic 18 L filter bed with CH_4 concentration of 0.15 to 1% v/v and gas flow rate of 0.06 to 0.42 $m^3.h^{-1}$. The concentrations of essential nutrients in NS were 0-1 $g.L^{-1}$ nitrogen, 0-6.2 $g.L^{-1}$ phosphorous, 0-3.8 $g.L^{-1}$ potassium and 0-0.006 $g.L^{-1}$ copper. It was reported that nitrogen had the greatest influence on BFs' performance. When nitrate (NO_3^-) concentration was increased from 0.14 to

0.75 $g.L^{-1}$, EC was increased more than 4 times at an IL of 95 $g.m^{-3}.h^{-1}$. The effect of phosphorous was less than nitrogen. An increase from 0.3 to 3.1 $g.L^{-1}$ in the concentration of phosphorous led to a 35% increase in EC at a CH_4 IL of 75 $g.m^{-3}.h^{-1}$. Nevertheless, high concentrations of phosphorus (i.e. more than 3.1 $g.L^{-1}$ in Nikiema's study [162]) would increase biomass growth rates, which in long runs might lead to clogging issues and RE decline. Hence, a concentration of 1.5 $g.L^{-1}$ was reported to be convenient in order to avoid the rapid clogging of CH_4 BF. The influence of variations in copper (Cu) concentration in NS was ignorable. Although, the presence of copper in NS is necessary for activating catalytic enzyme in MB [95]. Calcium (Cu) and magnesium (Mg) played a minor role in CH_4 bioelimination [19].

Utilizing fresh NS every day causes higher cost for BF operation [129]. In addition, the NS effluent (leachate), drained from BFs, contains nutrients and biomass, thus, it is considered as wastewater and should be treated. Khabiri *et al*. [126] evaluated the performance of a CH_4 BF irrigated by recycled NS, followed by analyzing nutrients' consumption in NS supply tank. Performance of the BF with recycled NS was promising and similar to that with fresh NS (CH_4 RE of 60-70%), at CH_4 concentrations up to 1% (v/v), whereas leachate production was reduced by 80%. In addition, the BF with recycled NS was resistant to the absence of NS for a few days. However, there is a need for further research on NS addition strategies to decrease producing leachate. The period of adding NS and behavior of BF in case of a stop in NS addition (starvation) was another issue, which should be investigated for industrial applications of BFs. Ferdowsi *et al*. [123] studied starvations in three steps. Firstly, the BF was fed with 0.2% v/v CH_4 and 0.18 $m^3.h^{-1}$ air with no NS for two weeks. For the next two weeks, only tap water was injected to the filter, as the second step. Methane and air were still passing through the BF. Finally, NS and CH_4 streams were stopped for 4 weeks. A strong potential of their BF to overcome NS shortage was observed. However, the condition with no CH_4 and no NS was harsh and a remarkable decline in BF's performance was observed after restart (RE decreased from 70 to 10%). Hernández *et al*. [137] carried out biofiltration of 0.2 v/v CH_4 as encountered at WWTPs. The effect of ammonium (NH_4^+) supplied in the NS on CH_4 RE was studied in a range of 0 to 1 $gN.L^{-1}$ of NH_4^+. A CH_4 EC of 11 $g.m^{-3}.h^{-1}$ was obtained (RE of 62%), when 0.52 $gN.L^{-1}$ of NH_4^+ was used as nitrogen source in NS.

2.6.6 Packing Materials

Organic, inorganic and synthetic materials are used as filter bed in biofiltration process. Investigations on the nature of packing materials in CH_4 biofiltration process showed that inorganic materials outperform organic ones [153]. Regarding BFs with inorganic supports, inoculation is required.

For treating mass transfer limited components, i.e. CH_4, high specific surface area as well as adsorption properties of the packing material could enhance the process [156]. Packing materials should possess high porosity (82–98%) and high specific surface area [174, 196]. In a study conducted by Nikiema and Heitz [197] for a CH_4 IL of 90 $g.m^{-3}.h^{-1}$, EC of 17, 38 and 50 $g.m^{-3}.h^{-1}$ were obtained for inorganic packing materials with specific surface area of 470, 1250, and 1360 $m^2.m^{-3}$, respectively. Limbri *et al*. [136] worked on a BF packed with coal with no inoculation. Synthesized NS was added every 3 days. Maximum CH_4 EC of about 27 $g.m^{-3}.h^{-1}$ corresponding a CH_4 RE of about 20% was achieved at CH_4 inlet concentration of 1% (v/v) for an EBRT of 2.4 min (gas flow rate of 0.1 $m^3.h^{-1}$).

Regarding comparison between organic and inorganic supports, due to different CH_4 concentrations, along with different gas flow rates and inoculation procedures, the impact of packing materials on BFs' performance has not been thoroughly understood. Details on packing materials considered in different studies on CH_4 biofiltration were provided in Table 2.6 together with operating conditions and BFs' performance (RE and EC). For inorganic packed BFs studied by Girard *et al*. [128] and Veillette *et al*. [127], CH_4 RE of 43 and 54% were reported, respectively. While in similar operating conditions, Nikiema *et al*. [153] observed a CH_4 RE of 19% using an organic packed BF (compost). Despite the lower RE for CH_4, compost materials are widely used as filter beds in methanotrophic processes. An empirical relationship was developed by Mancebo *et al*. [198] to predict BFs' performance when packed with compost and Hood *et al*. [199] studied biofiltration of a gaseous mixture including CH_4, N_2O, CO_2 and NH_3 from swine slurry. The BF was packed by compost and wood chips and experiments were carried out over summer, autumn, and winter. During autumn, CH_4 RE was 49% (EBRT of 26 s) and in summer was 13% (EBRT of 13 s). It was concluded that a compost based filter bed would be more effective for CH_4+N_2O elimination, but wood chip as packing material would be more economical.

2.6.7 Presence of trace compounds

Tolerances of BFs' performance to gases other than CH_4 should be taken into consideration as they might hinder microbial growth. Gaseous emissions from WWTPs may contain trace amounts of VOCs and VICs, such as CH_3OH, C_2H_5OH, C_8H_8, C_6H_6, H_2S, SO_2 and N_2O. Volatile organic compounds are frequently detected compounds in raw wastewater [200]. In commercialization overview, the dynamic behavior of BFs is important. For a unit in a WWTP, it is very common to produce pollutants with different characteristics (i.e. mass transfer and kinetic limited) as a mixture. For example, waste gas and wastewater from paint factories might contain a mixture of C_3H_6O, C_8H_8 and C_7H_8 in trace concentrations. Furthermore, wastewaters coming from some units of refineries and petrochemical complexes may carry a variety of VOCs. Although, the effect of some trace compounds were investigated before, the potential for these trace elements to affect CH_4 BF performance is still a challenging issue and needs more attention and investigation. Barcon *et al*. [201] investigated on simultaneous elimination of odors and CH_4 originated from a WWTP [202] in a BF with EBRT of 4 min. Mixed packing materials comprising a mixture of bark chips, perlite and compost were used with a volume ratio of 50, 35 and 15%, respectively. Gas flow rate was 0.1 $m^3.h^{-1}$ and CH_4 concentration was between 0.01 and 2.4% (average value of 1.25%). In spite of the fluctuations in the CH_4 inlet concentrations derived from the operation of WWTP, CH_4 RE of 77% (EC of 30 $g.m^{-3}.h^{-1}$) was achieved. Odor were eliminated by 99%. It was shown that the biomass developed in the WWTP was suitable as inoculum to start up the BF due to the presence of MBs.

Alcohols, especially CH_3OH and C_2H_5OH, as kinetic limited compounds are frequently produced in WWTPs due to the fermentation of fruit and vegetables, during the first stages of anaerobic digestion. When time passes, concentration of alcohol decreases and aldehydes and ketones are formed [203]. Mass transfer limited pollutants' removal could be more affected by the kinetic limited pollutants' concentration because kinetic limited pollutants are favorably soluble and biodegradable [156, 204]. Lebrero *et al*. [138] studied a compost BF to treat air containing 2% (v/v) CH_4 (mass transfer limited compound) in presence of CH_3OH (kinetic limited compound). An EC of 37 $g.m^{-3}.h^{-1}$ (RE of about 90%) was obtained for a high EBRT of 20 min. Comparing CH_3OH and C_2H_5OH, a methanol-based BF could display a better

performance for CH_4 conversion [205]. Ferdowsi *et al*. [206] treated C_2H_5OH (kinetic limited) and CH_4 (mass transfer limited) in an inorganic BF. Gas flow rates were increased from 0.2 to 0.7 $m^3.h^{-1}$ corresponding to EBRT of 6 to 1.5 min. For CH_4 ILs of 33 to 132 $g.m^{-3}.h^{-1}$ (CH_4/C_2H_5OH mass ratio of 7.5 $g.g^{-1}$), CH_4 REs dropped from 35 to 0% at C_2H_5OH ILs of 4.5 to 18 $g.m^{-3}.h^{-1}$, respectively. The lowest gas flow rate of 0.2 $m^3.h^{-1}$ (EBRT of 6 min) led to the best performance (CH_4 IL of 33 $g.m^{-3}.h^{-1}$ and C_2H_5OH IL of 4.5 $g.m^{-3}.h^{-1}$). Although, the presence of C_2H_5OH in the biofilm was reported to hinder the removal of CH_4.

The origin of aromatic compounds like C_7H_8 and C_8H_{10} in gaseous emissions from wastewaters is usually due to their use as solvents in paints, paint thinners and nail varnishes. Benzene and alkyl-substituted derivatives (i.e. C_8H_{10}) are also used in pesticides, varnishes, adhesives and paints [207]. Investigations by Ménard *et al*. [208] showed that an inhibition occurs in CH_4 biodegradation when C_7H_8 is accompanying CH_4 into the BF. The maximum CH_4 EC decreased from 40 to 6 $g.m^{-3}.h^{-1}$ when C_7H_8 concentration was increased from 0 to 3.4 $g.m^{-3}$. The experiments were carried out at different CH_4 concentrations of 0.2-0.9% (v/v). The presence of chlorinated organic compounds were also reported to be related to utilization of solvents such as cleaners and disinfectants from urban and industrial sources [209]. Other potential sources are aerosols, paint removers, dyeing solvents, foam blowing agents and paints [210], which mostly find their ways to sewer networks [211]. Few studies also confirmed the presence of terpenes with limonene and a-pinene among the trace elements. Household detergents were reported to be the origin of terpenes emission [212].

More research should be carried out on the ability of MBs regarding their resistance towards dynamic environmental stresses such as fluctuating inlet CH_4 concentrations, temporal and seasonal variations, competition among MOs for substrates and the co-metabolism due to the presence of other volatile compounds. Especially, the effect of H_2S on activities of MBs needs more consideration, since H_2S always accompanies CH_4 in waste gases emitting from WWTPs.

2.7 Conclusion

An important source of GHG emissions is related to WWTPs. In the current paper, a brief review of CH_4 emission from municipal and industrial wastewaters and sewage systems was provided. Methane was mainly produced in anaerobic digesters of WWTPs and in sewer biofilms and

sediments in rising main and gravity sewers. Methane from SNWs was detected at pumping stations and manholes with concentrations up to 5% v/v. A part of this paper focused on different bioreactors for the treatment of polluted air with CH_4. Biofilters are frequently used for waste gas treatment and wastewater treatment and are feasible to be used at full scales. Many aspects of CH_4 biofiltration are still not clear, especially in regards to bioreaction optimization for long-term operations. Another part of the paper reviewed the biofiltration of CH_4 and parameters effecting the BFs' performance, such as packing material, temperature, moisture and CH_4 concentration. Studies on biofiltration of CH_4 and VOCs/VICs mixtures originated in WWTPs and their interactions showed that aromatics and alcohols to be inhibitors of CH_4 bio-oxidation. Future research should focus on simultaneous waste gas/water biofiltration and parameters affecting CH_4 removal in this innovated system. In addition, more detailed and comprehensive field data should be provided for CH_4 emission from WWTPs to provide a better perspective for industrial applications. Applying cost-effective (bio-)chemicals in order to prevent the formation of CH_4 in SNWs and WWTPs' digesters is an alternative for GHG mitigation. Preventing CH_4 emissions from the liquid phase (i.e. denitrification process with CH_4 as the electron donor) could be an alternative. On the other hand, the possibility of valorization and energy provision must be investigated. The produced CH_4 could be recovered as biogas to be used as an energy source for the plant, if CH_4 concentration is high enough to make valorization a feasible approach.

CHAPTER 3 Different strategies of nutrient addition for methane biofiltration

Avant propos:

L'article "Methane biofiltration under different strategies of nutrient solution addition*"* a été publié dans le journal "Atmospheric Pollution Research" Volume 11, Issue 1, January 2020, Pages 85-93.

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Titre: Biofiltration du méthane : utilisation d'une solution nutritive recyclée

Title: Methane biofiltration under different strategies of nutrient solution addition

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Contribution to the document: This paper is relevant to the second objective of the thesis. Two CH_4 biofilters with the same packing materials and under the same operating conditions, one with fresh and the other one with recycled nutrient solution were evaluated and compared concerning the production of wastewater (leachate) from the bottom of the biofilters. In addition, performance of two biofilters were compared and discussed during starvation.

Methane biofiltration under different strategies of nutrient solution addition

3.1 Résumé

Deux biofiltres B1 et B2 remplis de matériaux inorganiques ont été exploités pendant 283 jours pour éliminer le méthane, un important gaz à effet de serre. Les biofiltres ont fonctionné avec un temps de résidence en fût vide constant (EBRT) de 6 min et des charges d'entrée (IL) de CH_4 de 7 à 63 $g.m^{-3}.h^{-1}$. B1 a été alimenté chaque jour avec une nouvelle solution nutritive (NS) (2 $L.d^{-1}$, débit volumique de 1 $L.min^{-1}$) tandis qu'une NS recyclée à partir d'un réservoir de 10 L a été fourni au B2. L'analyse du lixiviat présent dans le réservoir de recyclage a montré que l'utilisation d'une IL de 63 $g.m^{-3}.h^{-1}$ entraine une importante consommation de nutriments. Une conversion moyenne de CH_4 de 66±4% en utilisant une IL de 13 $g.m^{-3}.h^{-1}$ a été obtenue dans B1. Le biofiltre B2 s'est comporté de manière appropriée avec une conversion moyenne de 62±3% pour la même IL que B1, confirmant que la stratégie de recyclage est une approche prometteuse pour l'ajout de NS dans les biofiltres de CH_4.

Mots-clés: Biofiltration, Méthane, Méthode de recyclage, Solution nutritive, Consommation de nutriments, Privation de microorganismes.

3.2 Abstract

Two biofilters B1 and B2 packed with inorganic materials were operated for 283 days to eliminate methane (CH_4), an important greenhouse gas. The biofilters ran under a constant empty bed residence time (EBRT) of 6 min at CH_4 inlet loads (ILs) of 7 to 63 $g.m^{-3}.h^{-1}$. B1 was fed with a fresh nutrient solution (NS) every day (2 $L.d^{-1}$, flow rate of 1 $L.min^{-1}$) whereas B2 was supplied by a recycled NS from a 10 L tank. Analysis of NS in the recycle tank showed that the highest nutrient consumption over the time was at an IL of 63 $g.m^{-3}.h^{-1}$. B1 showed an average removal efficiency (RE) of 66±4% for an IL of 13 $g.m^{-3}.h^{-1}$. Biofilter B2 performed appropriately with an average RE of 62±3% for the same IL as B2, which confirmed that recycling strategy is a promising approach for NS addition in CH_4 biofilters.

Keywords: Biofiltration, Methane, Recycling method, Nutrient solution, Nutrients' consumption, Starvation.

3.3 Introduction

Methane (CH_4) is a colorless and odorless greenhouse gas (GHG) with global warming potency (GWP) of 25 times more than carbon dioxide (CO_2) [213]. The total GHGs' concentration in atmosphere has been reported to be increasing during the last 200 years and among GHGs, CH_4 atmospheric concentration was reported to be increasing at a rate of 0.02 ppmv per year [17]. There is a global consensus, i.e. COP21 (France 2015), COP22 (Morocco 2016), COP23 (Germany 2017), COP24 (Poland 2018) and COP25 (Spain 2019) aiming to achieve reduction of GHG emissions, along with considering limitations to prevent the production of GHGs from potential sources, in order to a 40% depletion in CO_2 equivalent emissions until 2030 [1].

Methane is naturally emitted to the atmosphere from wetlands, oceans, and plant degradation, accounts for about 40% of global CH_4 emissions, while anthropogenic sources like the energy sector, natural gas refineries, landfills, wastewater treatment plants, coal mining, and agriculture are responsible for 60% of CH_4 emissions [214]. Chemical oxidation, such as flaring or incineration, may be reasonable approaches to reduce CH_4 if its concentration is more than 5% (v/v). At lower CH_4 concentrations (under 5% (v/v)) these processes are uneconomical. Biological techniques are more reliable at lower CH_4 concentrations. Among bioprocesses, biofiltration has been a feasible alternative to non-biological approaches for air polluted with CH_4 [29, 62, 127, 214, 215]. Biofiltration is a bioprocess that eliminates CH_4 by the use of methanotrophic microorganisms (MOs) [127]. In biofilters, air polluted with CH_4 passes through a humidified bed, which is packed with organic/inorganic/synthetic materials. A liquid layer (biofilm) with MOs is present around the packing particles [216]. Methane is transferred from gas phase to biofilm and then, CH_4 biological transformation into biomass and products takes place, which are the main steps of biofiltration. Generally, water (H_2O), CO_2 and biomass are the main biodegradation products [156].

In CH_4 biofiltration, the pollutant (CH_4), itself, is considered the main substrate for MOs [94]. However, MOs need nutrients such as nitrogen, phosphorus and sulfur to break down CH_4. In a biofilter when these essential nutrients are in short supply, MOs may not be able to grow and divide appropriately [19, 153, 195]. To avoid this, a nutrient solution (NS) is usually added from the top of the biofilters. The effluent drained (leachate) from the bottom of the biofilter is considered as a wastewater, containing biomass, salts and a very low concentration of CH_4.

There is a need for research on alternative strategies of NS addition in biofilters to decrease the use of fresh NS, which would end up reducing the operational cost of NS provision and leachate treatment.

Since providing NS for biofilters is an important operating cost [129], the amount of required NS and addition method are considered as a challenge for developing CH_4 biofiltration technology. Daily addition of NS to CH_4 biofilters were frequently reported [123, 217-219]. To avoid regularly adding fresh NS (in order to decrease the costs), few studies used organic packings along with inorganic packings, simultaneously, to provide nutrients naturally and keep the pressure drop low at the same time [129], although, irrigation might be needed occasionally. In addition, bed drying, cracking and channeling as well as excess pressure drop might be other limitations when using organic packing materials [215]. Varying the composition of NS was another way to reduce the use of nutrients in the solution [127, 137]. Avoiding excess amount of nutrients in NS, results in lower chemical contents in leachate, which makes it easier to deal with the wastewater leaving the biofilter.

Stopping nutrient addition for several days was also investigated in order to examine the tolerance of biofilters for nutrient starvation condition. Few works have reported the biofilters resistance for even 2 weeks without NS addition [123, 197, 220]. Some studies discussed about the flow rate of NS addition in biofilters. Hernández *et al*. [137] added fresh NS to a CH_4 biofilter with a low flow rate of 0.066 $L.min^{-1}$ during 5 min every day (0.33 $L.d^{-1}$). The same NS flow rate was also used by Gomez-Cuervo [221] for treating diffuse CH_4 emissions in organic and inorganic packed bed biofilters. It was reported that adding NS with a low flow rate led to a complete distribution of NS through the bed and produced a low quantity of wastewater.

Efforts are still required to make biofiltration process cost-effective; therefore, other methods related to NS addition like NS recycling as well as the effect of the frequency of NS addition and nutrient starvation should be examined. Recycling NS in biofilters could be a feasible way to reduce the nutrient consumption while the biofilter is performing properly. Moreover, leachate production could be reduced by the recycling approach, which means that smaller amount of wastewater would be drained from the biofilter and later wastewater treatments might be less expensive. To our best knowledge, there is no study on recycling NS in biofilters. Different strategies of NS addition might also influence the filter bed pressure drop. For

example, under recycling methods or starvation, a reduced pressure drop is expected since MOs are exposed to less nutrients and less biomass should be produced in the filter bed [222-224]. This study evaluates the performance of a lab-scale biofilter for CH_4 removal from polluted air by means of different NS addition strategies. Adding a certain amount of fresh NS every day, recycling NS, adding NS in portions (i.e. several times a day) and no NS addition were investigated. The effect of CH_4 inlet concentrations on the biofilter performance was also studied during different NS addition conditions. Finally, concentrations of nitrate (NO_3^-), sulfate (SO_4^{2-}) and phosphate (PO_4^{3-}) in leachate were studied to compare the consumption of the nutrients.

3.4 Materials and methods

3.4.1 Lab-scale biofilter set-up

Two 18 L Plexiglas lab-scale biofilters (Figure 3.1) were used, with 1 m height and an interior diameter of 0.15 m. Each biofilter contained 3 sections and each bed had one port for gas measurement (e.g., CO_2, CH_4). Both biofilters were packed with non-porous inorganic materials with an average diameter of 5×10^{-3} m. A mixture of CH_4 (Praxair Inc., Canada) and humidified air was injected at the bottom of the biofilter, representing the contaminated air. Humidification of air was achieved by passing the air stream through a bubbler humidifier (diameter = 0.10 m and length 0.75 m). All flow rates were adjusted by mass flow controllers (Brooks, USA).

3.4.2 Analytical tools

Methane concentration was measured by a total hydrocarbon flame ionization analyzer (FIA 510, Horiba, Japan). A CO_2 gas analyzer (Ultramat 22P, Siemens, Germany) was used to measure CO_2 concentration. Filter bed's pressure drop was measured by means of a differential manometer (Air Flow Developments, UK) with an accuracy of 0.01 $cmH_2O.m^{-1}$. An ion chromatography system (ICS-1000, Dionex, USA) was used for analyzing the composition of nitrate (NO_3^-), phosphate (PO_4^{3-}) and sulfate (SO_4^{2-}) in leachate.

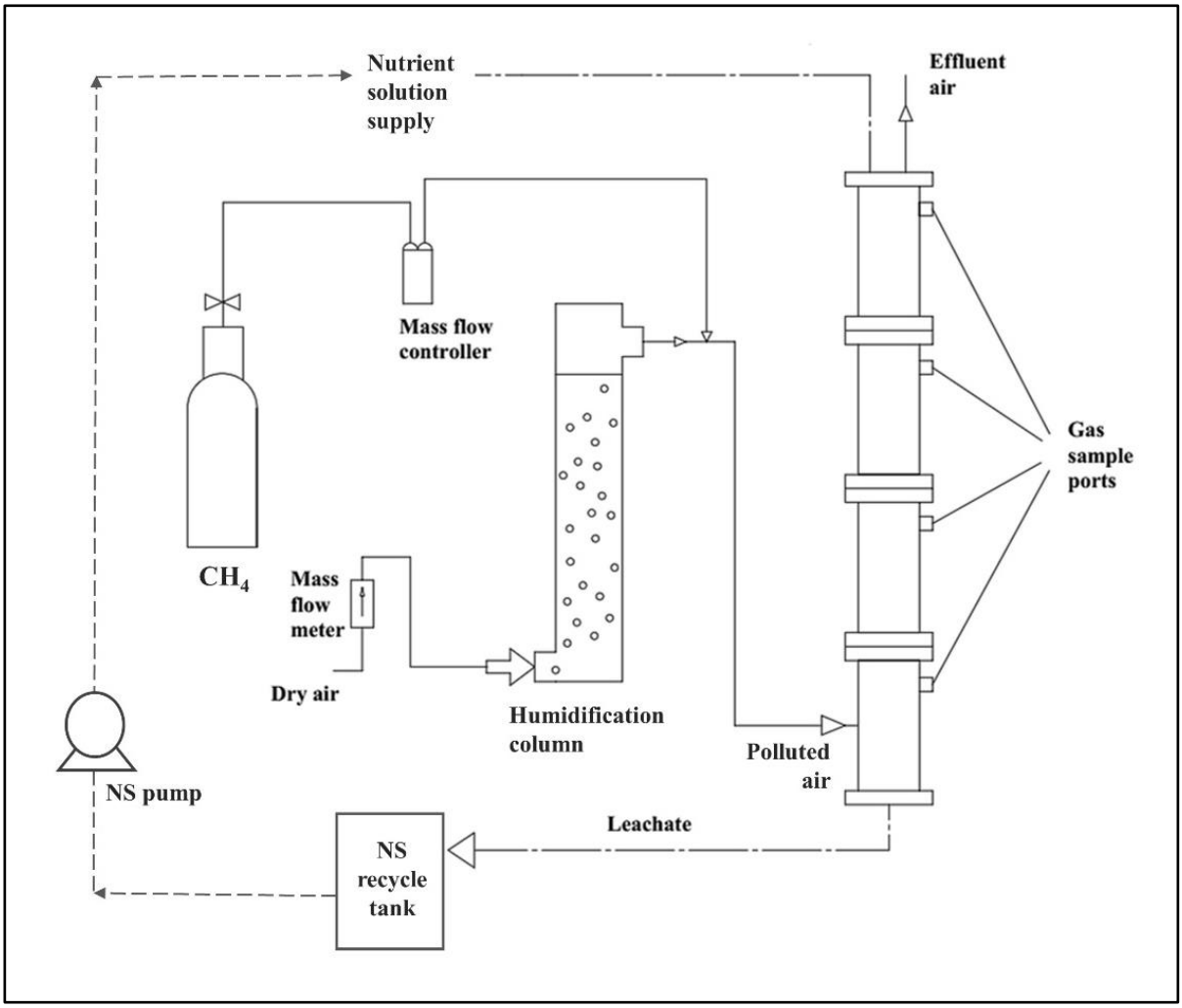

Figure 3.1: Schematic of the lab-scale biofilters

3.4.3 Performance parameters and equations

In order to evaluate each biofilter's performance, the following equations were used:

$$\text{Inlet load (IL)} = \frac{C_{(CH_4)in} \times Q}{V} \quad (g.m^{-3}.h^{-1}) \quad (1)$$

$$CH_4 \text{ removal efficiency (RE)} = \frac{C_{(CH_4)in} - C_{(CH_4)out}}{C_{(CH_4)in}} \quad (\%) \quad (2)$$

$$\text{Elimination capacity (EC)} = IL \times RE \quad (g.m^{-3}.h^{-1}) \quad (3)$$

$$CO_2 \text{ production rate } (PCO_2) = \frac{\left(C_{(CO_2)out} - C_{(CO_2)in}\right) \times Q}{V} \quad (g.m^{-3}.h^{-1}) \quad (4)$$

Where $C_{(CH_4)in}$ and $C_{(CH_4)out}$ are the CH_4 inlet and outlet concentrations ($g.m^{-3}$), respectively. $C_{(CO_2)in}$ and $C_{(CO_2)out}$ are the CO_2 inlet and outlet concentrations ($g.m^{-3}$), respectively. Q is the gas flow rate in $m^3.h^{-1}$ and V is the bed volume in m^3.

3.4.4 Experimental methods and conditions

After washing the packing thoroughly with tap water, 5 L of the leachate from an active CH_4 biofilter (RE≈65%, IL=30 $g.m^{-3}.h^{-1}$) was introduced to each biofilter from the top and recycled 3 times (same day) in order to inoculate the biofilters. Meanwhile, the contaminated air (mixture of CH_4 and humid air) was passing through the biofilter. Air flow rate was fixed at 0.18 $m^3.h^{-1}$ and empty bed residence time (EBRT) was 0.1 h. Biofilter 1 (B1) was exposed to fresh NS every day whereas biofilter 2 (B2) was fed from a 10 L recycle tank. Composition of the fresh NS is described in Table 3.1.

The concentrations of NO_3^-, PO_4^{3-} and SO_4^{2-} in fresh NS as well as the initial concentrations of NO_3^-, PO_4^{3-} and SO_4^{2-} in the recycle tank were 2200, 980 and 110 $mg.L_{NS}^{-1}$, respectively. During the acclimation period, biofilters ran for 2 weeks at 1000 ppmv CH_4 concentration to allow adequate time for microbial growth.

The experiments were divided into 7 phases as shown in Table 3.2 and effects of recycling NS, starvation period and frequent addition of NS were investigated. The phases were based on CH_4 inlet concentration variation. Experiments were conducted at 5 different CH_4 concentrations of 1000, 2000, 4500, 7000, 9500 ppmv, corresponding to ILs of 7, 13, 30, 46 and 63 $g.m^{-3}.h^{-1}$ in each biofilter. It should be noted that NS in the recycle tank of B2 was refreshed at the beginning of each phase.

In phase 1-5 and 7, NS was added to B1 and B2 with a liquid flow rate of 1 $L.min^{-1}$. In phase 1-5, 2 L of NS was added during 2 min every 24 hours. While, in phase 7, 0.5 L of NS was added during 0.5 min every 6 hours (frequent NS addition) in order to investigate the effect of injecting NS in portions (CH_4 concentration of 9500 ppmv).

Table 3.1: Composition of fresh nutrient solution provided for B1 and B2

Components	**Formula**	**$mg.L^{-1}_{NS}$**
Sodium nitrate	$NaNO_3$	3024
Disodium phosphate	Na_2HPO_4	860
Monopotassium phosphate	KH_2PO_4	530
Potassium sulfate	K_2SO_4	170
Magnesium sulfate heptahydrate	$MgSO_4.7H_2O$	37
Calcium chloride dihydrate	$CaCl_2.2H_2O$	7
Manganese sulfate heptahydrate	$MnSO_4.7H_2O$	0.5
Zinc sulfate heptahydrate	$ZnSO_4.7H_2O$	0.6
Ferrous sulfate heptahydrate	$FeSO_4.7H_2O$	0.1
Copper sulfate pentahydrate	$CuSO_4.5H_2O$	0.3
Potassium iodide	KI	0.2
Boric acid	H_3BO_3	0.1
Cobaltous chloride hexahydrate	$CoCl_2.6H_2O$	0.1
Sodium molybdate dihydrate	$NaMoO_4.2H_2O$	0.1

In phase 6, both biofilters were exposed to a starvation period to investigate on biofilter tolerance in lack of nutrients at 9500 ppmv CH_4 inlet concentration. During starvation, polluted air was passing through the biofilters for 1 month, without adding any NS to the biofilters.

During all phases, concentrations of CH_4 and CO_2 were measured every two days and leachate samples were collected weekly to investigate on consumption of nutrients in NS.

Table 3.2: Operating conditions in B1 and B2

Biofilters	Phase 1	Phase 2	Phase 3	Phase 4.1	Phase 4.2	Phase 4.3	Phase 4.4	Phase 4.5	Phase 5	Phase 6	Phase 7
	Acclimation				Shutdown		Shutdown			Starvation (No NS added)	Frequency of NS addition
Duration (d)	14	30	30	10	15	30	30	20	30	35	35
Operating days	1-14	15-45	46-75	76-85	86-100	101-130	131-160	161-180	181-210	211-247	248-283
Methane inlet concentration (ppmv)	1000	2000	4500	7000	-	7000	-	7000	9500	9500	9500
Methane inlet load ($g.m^{-3}.h^{-1}$)	7	13	30	46	-	46	-	46	63	63	63
NS ($L.d^{-1}$)	2	2	2	2	-	2	-	2	2	-	4 * 0.5

Notes:
V = 0.018 m^3 , Q = 0.18 $m^3.h^{-1}$, EBRT = 0.1 h, NS flow rate = 1 $L_{liq}.min^{-1}$
NS: nutrient solution , EBRT: empty bed residence time, Q: air flow rate, V: volume, d: day
Concentrations of nutrients in fresh NS: NO_3^- = 2200 $mg.L_{NS}^{-1}$, PO_4^{3-} = 980 $mg.L_{NS}^{-1}$ and SO_4^{2-} = 110 $mg.L_{NS}^{-1}$

3.5 Results and discussion

3.5.1 The performance of the biofilters B1 and B2

Figure 3.2 presents the effect of CH_4 IL on biofilters performance in terms of RE while the EBRT was fixed at 0.1 h. During acclimation period (phase 1), both biofilters reached a RE of about 55% for CH_4 IL of 7 $g.m^{-3}.h^{-1}$. By increasing CH_4 IL from 7 to 63 $g.m^{-3}.h^{-1}$, RE first increased to a peak of 66±4% (IL=13 $g.m^{-3}.h^{-1}$) and 67±3% (IL=30 $g.m^{-3}.h^{-1}$) for B1 and B2, respectively. Removal efficiencies then decreased gradually to 57±4 and 49±4% for CH_4 IL of 63 $g.m^{-3}.h^{-1}$ in B1 and B2, respectively. This increasing-decreasing trend was due to a critical IL of 13 $g.m^{-3}.h^{-1}$ in B1 and 30 $g.m^{-3}.h^{-1}$ in B2. The critical ILs are representative of a transition state from a mass transfer limited to a kinetic limited regime, which are different from one biofilter to another, depending on the operating conditions of the biofilters, characteristics of the inoculum, nature of the packing materials, type of the pollutants and nutrients [225]. For ILs below critical IL (13 $g.m^{-3}.h^{-1}$ for B1 and 30 $g.m^{-3}.h^{-1}$ for B2), the removal of CH_4 was mostly limited by low bioavailability of CH_4 in the biofilm phase as a result of poor CH_4 diffusion from gas to the biofilm. Under mass transfer limited regime, increasing the CH_4 inlet concentration (gas phase) led to exceeding CH_4 concentration in the biofilm phase based on Henry's law and consequently the biofilters' performance was improved. In contrast, for ILs exceeding the critical IL (13 $g.m^{-3}.h^{-1}$ for B1 and 30 $g.m^{-3}.h^{-1}$ for B2), RE was influenced negatively by kinetic limitations (e.g., inhibition) due to excess bioavailability of CH_4 in biofilm [225].

Decreasing trend of CH_4 RE (from 30 to 20%) by increasing CH_4 IL (from 22 to 154 $g.m^{-3}.h^{-1}$) was also reported by Brandt *et al*. [129] for an EBRT of 0.12 h (mixture of organic and inorganic packing materials), which revealed a kinetic limited regime range of IL. A reduction in CH_4 RE (from 29 to 8%) was also observed in a coal packed biofilter with constant CH_4 concentration of 10000 ppmv, when IL increased (from 17 to 208 $g.m^{-3}.h^{-1}$) by means of increasing air flow rate (from 0.012 to 0.144 $m^3.h^{-1}$) [136]. This could indicate that increasing ILs, regardless of how IL increases, i.e. by increasing either CH_4 concentration or gas flow rate, led to a kinetic limited regime and RE reduction.

B2 reached about the same RE as B1 at CH_4 ILs lower than 30 $g.m^{-3}.h^{-1}$, which supported the NS recycling method for low CH_4 biofiltration. Nonetheless, for CH_4 ILs exceeding 30 $g.m^{-3}.h^{-1}$,

the CH_4 REs for B2 were lower than those for B1. For CH_4 IL of 46 and 63 $g.m^{-3}.h^{-1}$, REs were obtained as 54±5 and 48±4% for B2 and 60±6 and 57±4% for B1.

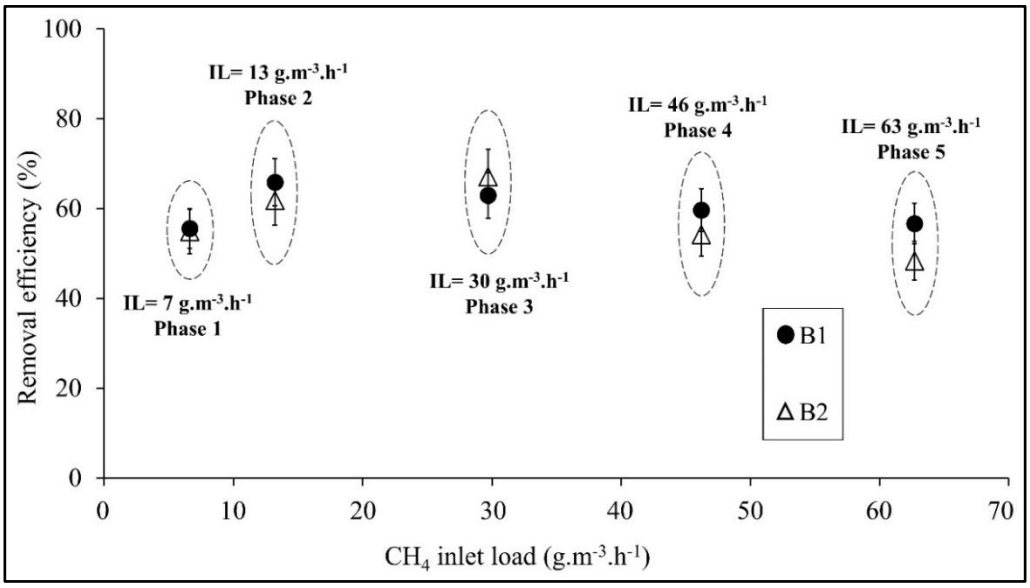

Figure 3.2: Removal efficiency of B1 and B2 as a function of CH_4 inlet concentration

An analysis of variance (ANOVA test) was performed to examine the level of significance for RE relative to B1 and B2. The statistical analysis was performed with Microsoft Excel 2016 and differences with a level of significance below 0.05 were considered as significant. For CH_4 ILs less than 30 $g.m^{-3}.h^{-1}$, for a confidence interval of 95%, there was no statistical difference of RE between B1 and B2 with significance level superior to 0.05 at two ILs of 7 and 30 $g.m^{-3}.h^{-1}$ ($p>0.05$). However, there was a significant difference at IL of 13 $g.m^{-3}.h^{-1}$ ($p<0.05$). In comparison with low ILs, difference of RE between B1 and B2 at high ILs of 46 and 63 $g.m^{-3}.h^{-1}$ was more significant with significance level of below 0.005 and 0.001, respectively ($p<0.005$ and $p<0.001$).

The RE difference between B1 and B2 could be due to the shortage of nutrients in B2's NS under kinetic limited regime. B1 was always exposed to fresh NS whereas B2 might be hampered by the shortage of essential nutrients (e.g., nitrogen, phosphorous). Although the performance of B1 is better compared to B2, the results for both biofilters in terms of RE_{max} are comparable and in the range of recent studies for CH_4 biofiltration [123, 129, 137, 219, 221].

Figure 3.3 shows EC versus CH_4 IL (ranging from 7 to 63 $g.m^{-3}.h^{-1}$) and the deviation from the 100% RE line. This range of ILs (7-63 $g.m^{-3}.h^{-1}$) was related to a concentration of 1000 to 9500

ppmv of CH_4 and an air flow rate of 0.18 $m^3.h^{-1}$. Elimination capacity demonstrated an ascending tendency in B1 and B2 when IL was increased. Elimination capacities were equal for B1 and B2 at ILs of 7 and 13 $g.m^{-3}.h^{-1}$ (EC = 4±1 and 8±1 $g.m^{-3}.h^{-1}$, respectively). At IL of 30 $g.m^{-3}.h^{-1}$, ECs were 19±1 and 20±1 $g.m^{-3}.h^{-1}$ for B1 and B2, respectively (about the same). At IL of 46 $g.m^{-3}.h^{-1}$, ECs were 28±3 and 25±3 $g.m^{-3}.h^{-1}$ for B1 and B2, respectively (about 10% of difference) and at IL of 63 $g.m^{-3}.h^{-1}$, ECs were 36±3 and 31±2 $g.m^{-3}.h^{-1}$ for B1 and B2, respectively (about 14% of difference). At higher ILs (more than 46 $g.m^{-3}.h^{-1}$), the ECs for B2 had more deviation from the 100% RE line than B1, probably due to kinetic limitations and less availability of nutrients for MOs.

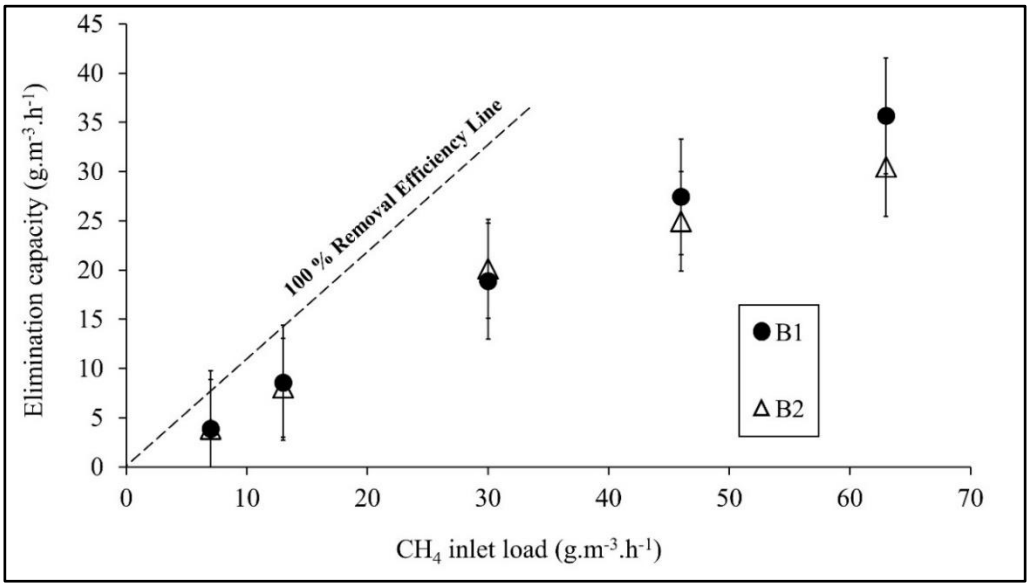

Figure 3.3: Elimination capacity of B1 and B2 as a function of CH_4 inlet loads

3.5.2 Variations of essential nutrient concentrations in recycle tank

Providing all sources of energy required by MOs is essential for biofiltration process. Methane is the primary substrate for MOs to stay biologically active. Nitrogen like NO_3^-, phosphorous like PO_4^{3-} and sulfur like SO_4^{2-} are the nutrients, which should be included in NS in a CH_4 biofilter [195]. Concentrations of nutrients in B1 are presented in Table 3.3. Variations of nutrients concentrations (e.g. NO_3^-, PO_4^{3-} and SO_4^{2-}) in B2 are shown in Table 3.4 as a function of time. In each phase, compared to B1, B2 was exposed to lower concentrations of nutrients depending on time (day) according to Table 3.4.

Table 3.3: Concentrations of nutrients ($mg.L_{NS}^{-1}$) in the NS for B1

Day	B1 CH_4 concentration	Nitrate (NO_3^-) $mg.L_{NS}^{-1}$	Phosphate (PO_4^{3-}) $mg.L_{NS}^{-1}$	Sulfate (SO_4^{2-}) $mg.L_{NS}^{-1}$
1-210	1000-9500 ppmv (IL= 7-63 $g.m^{-3}.h^{-1}$) Phases 1-5 and 7	2200	980	110

Table 3.4: Concentrations of nutrients ($mg.L_{NS}^{-1}$) in the NS for B2

Day	B2 CH_4 concentration	Nitrate (NO_3^-) $mg.L_{NS}^{-1}$	Phosphate (PO_4^{3-}) $mg.L_{NS}^{-1}$	Sulfate (SO_4^{2-}) $mg.L_{NS}^{-1}$
1	1000 ppmv (IL= 7 $g.m^{-3}.h^{-1}$) Phase 1	2200	980	110
8		2150	965	105
14		1750	950	70
15	2000 ppmv (IL= 13 $g.m^{-3}.h^{-1}$) Phase 2	2200	980	110
21		2000	925	80
29		1825	900	60
35		1600	850	35
45		1175	820	50
46	4500 ppmv (IL= 30 $g.m^{-3}.h^{-1}$) Phase 3	2200	980	110
51		1725	975	92
57		1350	750	61
66		1175	675	49
75		1095	400	33
101	7000 ppmv (IL= 46 $g.m^{-3}.h^{-1}$) Phase 4	2200	980	110
105		2425	810	116
113		1850	585	87
121		1200	385	56
130		625	260	30
181	9500 ppmv (IL= 63 $g.m^{-3}.h^{-1}$) Phase 5	2200	980	110
187		2150	580	90
195		1350	330	65
203		710	180	59
210		340	5	25

B1 with fresh NS was provided with constant concentrations of 2200, 980 and 110 mg.L_{NS}^{-1} for NO_3^-, PO_4^{3-} and SO_4^{2-}, respectively, for all phases every day. Regarding B2, at the beginning of each phase, initial concentrations of nutrients in the recycle tank were the same as B1 (2200 mg.L_{NS}^{-1}, 980 mg.L_{NS}^{-1} and 110 mg.L_{NS}^{-1} for NO_3^-, PO_4^{3-} and SO_4^{2-}, respectively). However, during each phase in B2, the concentrations of nutrients were diminishing over the time. For instance, in phase 5, at day 203, at IL=63 g.m^{-3}.h^{-1} (9500 ppmv), B2 was provided with NO_3^-, PO_4^{3-} and SO_4^{2-} concentrations of 710, 180 and 59 mg.L_{NS}^{-1} (68, 82 and 46% less than B1), respectively (as indicated in Table 3.4). Among the nutrients, more NO_3^- was consumed than PO_4^{3-} and SO_4^{2-}. Out of 2200 mg.L_{NS}^{-1} of the initial NO_3^- concentration, 21, 47, 50, 72 and 84% were consumed during phases 1 to 5, respectively.

Figure 3.4 shows the consumption of nutrients (NO_3^-, PO_4^{3-} and SO_4^{2-}) versus CH_4 ILs in B2. According to Figure 3.4 by increasing CH_4 IL from 7 to 63 g.m^{-3}.h^{-1}, consumption of NO_3^-, PO_4^{3-} and SO_4^{2-} increased linearly from 450 to 1860 mg.L_{NS}^{-1}, from 30 to 975 mg.L_{NS}^{-1} and from 40 to 85 mg.L_{NS}^{-1} respectively. The linear trends showed that the consumption increasing rate of NO_3^-, PO_4^{3-} and SO_4^{2-} could be considered proportional to CH_4 IL increase.

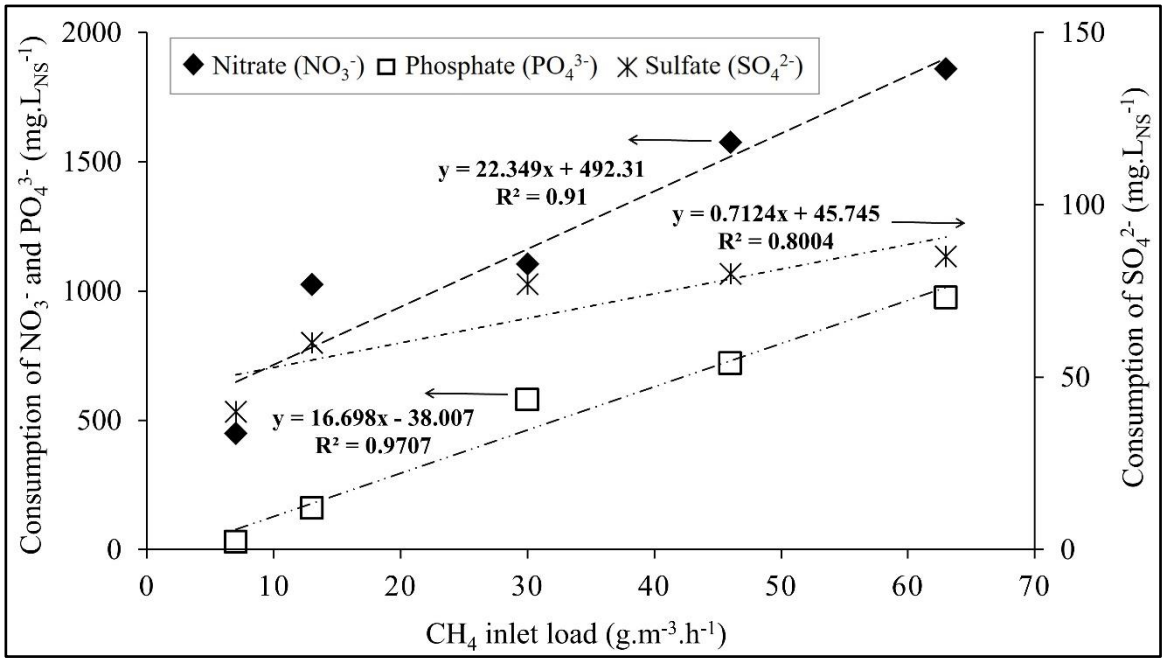

Figure 3.4: Consumption of nutrients in B2 as a function of CH_4 IL.

Initial concentrations of nutrients in NS:

NO_3^- = 2200 mg.L_{NS}^{-1}, PO_4^{3-} = 980 mg.L_{NS}^{-1} and SO_4^{2-} = 110 mg.L_{NS}^{-1}

The recycling method lowered the pressure drop in B2. After 5 months, pressure drop in B2 was 0.08 $cmH_2O.m^{-1}$, whereas in B1, pressure drop was 0.11 $cmH_2O.m^{-1}$. Lower pressure drop in B2 (about 30% lower than B1) could be due to the less amount of nutrients provided to B2 compared to B1. However, the difference in pressure drop was not significant.

3.5.3 Carbon dioxide production

Production of CO_2 (PCO_2) for B1 and B2 as a function of EC is shown on Figure 3.5. The carbon in CH_4 degradation could result in the production of CO_2 and biomass [173]. If there were no biomass, the mass ratio of PCO_2 to EC would be fixed to 2.75. Since biomass production was not inevitable, a deviation from stoichiometric (theoretical mass ratio) line was observed. At ILs of 7 to 63 $g.m^{-3}.h^{-1}$, CO_2 production increased from 9 to 61 $g.m^{-3}.h^{-1}$ for EC of 4 to 36 $g.m^{-3}.h^{-1}$ in B1 and from 9 to 54 $g.m^{-3}.h^{-1}$ for EC of 4 to 31 $g.m^{-3}.h^{-1}$ in B2. Similar results were reported by Limbri et al. [136] when a 4 L lab-scale biofilter packed with coal was used for CH_4 removal with ILs ranging from 17 to 208 $g.m^{-3}.h^{-1}$ (NS was supplied every 3 days). Deviation from the stoichiometric line for PCO_2 versus CH_4 EC, was also confirmed by Ferdowsi et al. [123] (ILs=13-65 $g.m^{-3}.h^{-1}$ and EBRT=0.1 h) and Veillette et al. [127] (IL=20 $g.m^{-3}.h^{-1}$ and EBRT=0.1 h). As the mean ratio of PCO_2/EC decreased from 2.2 to 1.7 by increasing IL, it could be concluded that by increasing CH_4 ILs, a bigger portion of biomass could be expected in biodegradation products [226].

Figure 3.6 illustrates the relationship between EC and PCO_2 as a function of NO_3^- consumption in the recycle tank for B2. At CH_4 ILs of 7, 13 and 30 $g.m^{-3}.h^{-1}$ (low CH_4 concentrations), the amount of consumed NO_3^- were 450, 1025 and 1105 $mg.L_{NS}^{-1}$, respectively, corresponding to ECs of 4, 8 and 20 $g.m^{-3}.h^{-1}$ and PCO_2 of 8, 18 and 38 $g.m^{-3}.h^{-1}$, respectively. At ILs of 46 and 63 $g.m^{-3}.h^{-1}$ (higher concentrations of CH_4), B2 showed higher EC of 23 and 31 $g.m^{-3}.h^{-1}$, higher PCO_2 of 48 and 53 $g.m^{-3}.h^{-1}$ and higher NO_3^- consumptions of 1575 and 1860 $mg.L_{NS}^{-1}$, respectively, compared to lower ILs. According to Figure 3.6, more NO_3^- was used at higher ILs and lower PCO_2/EC was obtained.

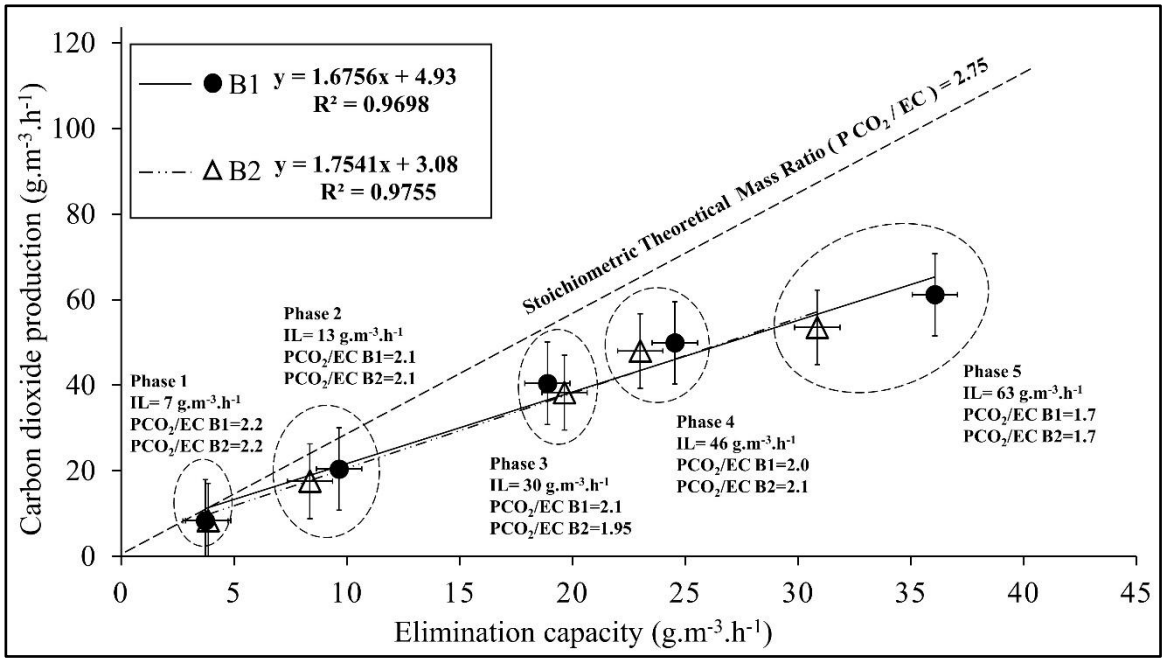

Figure 3.5: Carbon dioxide production for B1 and B2 as a function of elimination capacity

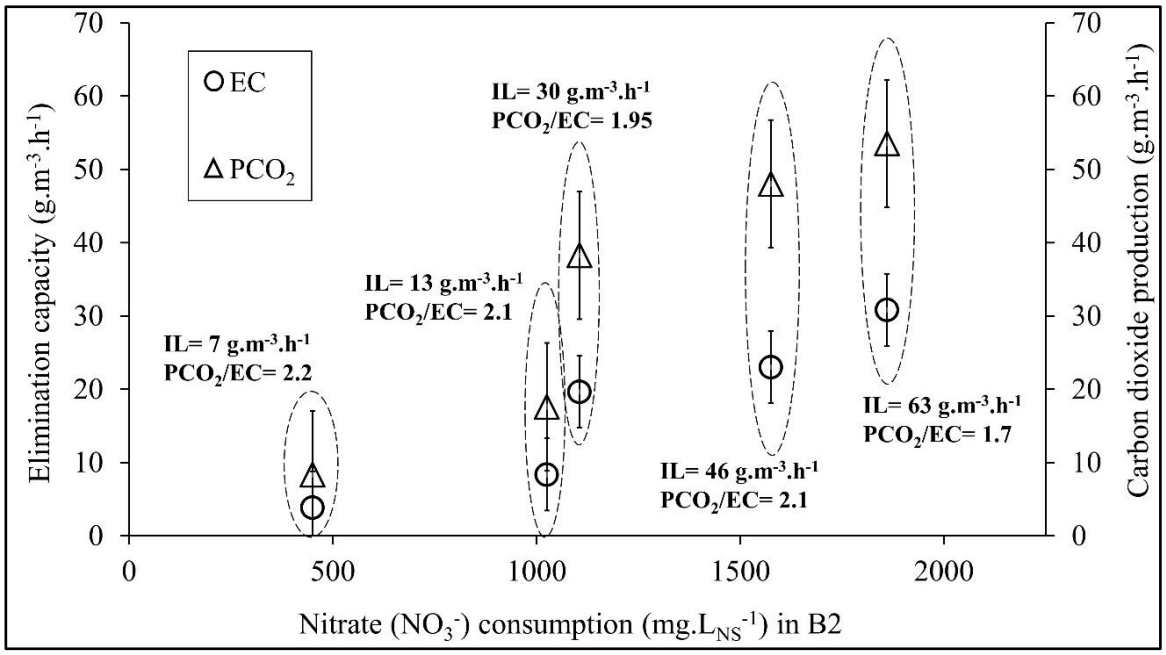

Figure 3.6: Elimination capacity and carbon dioxide production as a function of nitrate consumption in B2

3.5.4 Performance during starvation period and frequent NS addition

Figure 3.7 shows RE of B1 and B2 at 9500 ppmv CH_4 using different strategies of NS addition: a. 2 $L.d^{-1}$ (phase 5), b. Starvation (phase 6), c. 4*0.5 $L.d^{-1}$ (phase 7). Phase 5 started after 20 days of biofiltering 7000 ppmv CH_4 with 2 $L.d^{-1}$ NS addition and phase 7 started after 35 days of biofiltering 9500 ppmv CH_4 with no external NS (starvation). In phase 5, RE increased to 61% (day 199) and maintained constant around 59% until day 211 in B1 (with an average RE of 57±4%). For B2, RE reached a peak of 58% (day 197) and then gradually decreased until day 207 to reach 47% (average RE of 48±4%). Although recycling the NS ended up with a lower RE in B2, the B2 still performed appropriately (an average RE of 48±4% for B2 compared to B1 with an average RE of 57±4%).

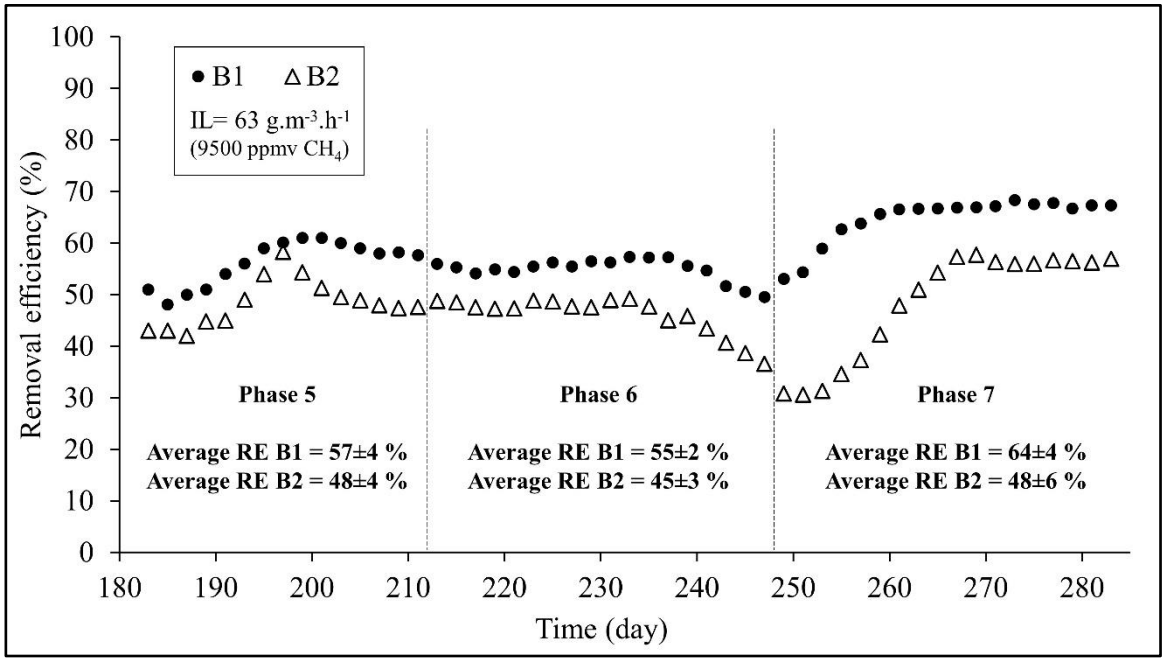

Figure 3.7: Removal efficiency of B1 and B2 during phases 5, 6 and 7 as a function of time

In phase 6, both biofilters were confronted with nutrient starvation conditions (days 213-247). For B1, RE stayed almost constant (58%) up to day 237 and then decreased gradually to 49% (day 247). For B2, RE maintained constant (48%) until day 233 and then declined to 36% (day 247). The 15% RE decrease in B1 after day 237 and 26% decrease in B2 after day 233 might have been occurred by a shortage in essential nutrients, which led to less activity of MOs. During

the starvation period, pressure drop decreased from 0.12 to 0.03 $cmH_2O.m^{-1}$ for B1 and from 0.11 to 0.04 $cmH_2O.m^{-1}$ for B2 (75% decrease for B1 and 63% for B2) probably because of biomass diminution. Imposing occasional starvation conditions to a biofilter was introduced as an approach to control biomass accumulation and prevent clogging, therefore, the biofilter could perform longer [213, 227, 228]. During starvation (a shortage in external nutrient supply), MOs could survive and continue CH_4 biodegradation, probably because they could use biomass as a source of nutrient, which led to biomass diminution in the filtering bed and consequently, reduction in pressure drop [220]. In this situation, cell division occur slowly [229]. The MOs' population might have stopped to divide, but remained active [230].

Lisovitskaya *et al*. [172] ran a semi-batch organic (soil-like) packed CH_4 biofilter during winter in Moscow (V = 20 L), with no extra NS addition. A RE of 53% was achieved at a high CH_4 concentration of 25000 ppmv, which is comparable to RE in B1 and B2 during starvation (55% for B1 and 45% for B2). Nikiema et al. [197] imposed starvation condition to a biofilter with a gas flow rate of 0.33 $m^3.h^{-1}$ and a CH_4 concentration of 2300 ppmv. Removal efficiency decreased about 40% in 18 days. The RE decline was higher than the ones obtained for B1 and B2 (15% RE decrease in B1 and 26% decrease in B2). At lower CH_4 concentrations (i.e. 2300 ppmv [197]), MOs type I are dominant in filter bed, and at higher CH_4 concentrations (i.e. 25000 ppmv [172] and 9500 ppmv), MOs type II are dominant [231]. Type I are deactivated quickly during starvation conditions (lack of nutrient supply for MOs in CH_4 biofiltration), but type II are not sensitive to nutrient limitation and can persist longer [124, 232]. In case of starvation in a biofilter with high CH_4 concentration (i.e. 25000 ppmv [172]), biofilters could resist and perform promisingly for a longer duration, compared to starvation at low CH_4 concentration (i.e. 2300 ppmv [197]). That might be the reason why B1 and B2 performed adequately during phase 6.

In phase 7, RE in B1 began to increase immediately and reached about the same RE, as before the starvation period (58%) in 5 days (days 249-253). The ascending trend remained until B1 reached about 67% RE (day 259) and stayed almost constant, indicating a pseudo steady state condition in B1 after 10 days. In B2, the descending tendency in RE continued until day 251, where RE reached 30%. After that, RE increased to the same RE as before starvation (48%) in day 261 and reached a pseudo steady state after 18 days with a RE of 57% in day 267 (days 249-267). Frequent addition of NS in phase 7, provided adequate time for MOs to uptake

the essential nutrients [233], as NO_3^- and PO_4^{3-}. Shorter time for B1 and B2 to reach pseudo steady state in phase 7 (10 days for B1 and 18 days for B2), in comparison to phase 5 (18 days for B1 and 20 days for B2), could be due to NS accumulation and humidity (water accumulation) of filter bed in phase 5 [135]. Adding NS of 2 $L.d^{-1}$ in 2 minutes might have imposed water accumulation in B1 and B2 during phase 5. Water accumulation in beds has negative effects on RE, since it limits the transfer of CH_4 to biofilm. Water accumulation also causes channeling which leads to bypassing of MOs [95]. That could be the reason why average RE in phase 7 (64%) was higher than in phase 5 (57%) for B1. However, no remarkable difference was observed in average RE for B2 in phases 5 and 7.

Comparing REs of B1 and B2 during phases 5, 6 and 7 (different NS addition conditions) revealed that recycling NS could be practical in CH_4 biofiltration. In both B1 and B2, the lowest RE were observed during starvation in phase 6 (55% and 45%, respectively). Adding NS in small portions in phase 7 (0.5 L every 6 h), generally led to a better performance, i.e. a higher RE and a shorter time to reach pseudo steady state for B1 and B2.

3.6 Conclusion

The influence of recycling NS in a CH_4 biofilter (B2) was investigated and compared to fresh NS addition (B1). Effects of a) increasing CH_4 IL from 7 to 63 $g.m^{-3}.h^{-1}$ b) the consumption pattern of nutrients in NS recycle tank, c) starvation conditions as well as d) frequency of NS addition were also investigated. Maximum REs of 66±4% (IL of 13 $g.m^{-3}.h^{-1}$) and 67±3% (IL of 30 $g.m^{-3}.h^{-1}$) were obtained for B1 and B2, respectively. In general, lower performance of B2 compared to B1 could be linked to the reduction of essential nutrients (e.g., NO_3^-, PO_4^{3-} and SO_4^{2-}) in the recycle tank over the time. Among nutrients, nitrate (NO_3^-) displayed the maximum consumption. Biofilters B1 and B2 tolerated nutrient starvation for about 3 weeks (constant RE of 58 and 48%, respectively) and then, a RE reduction of 15% and 26% was observed, respectively, for a corresponding IL of 63 $g.m^{-3}.h^{-1}$. Based on average RE of B1 (55±2%) and B2 (45±3%), both biofilters performed reliably during 35 days of NS starvation. The frequency of NS addition was also studied (2 L per 24 h and 0.5 L per 6 h). Better performance (RE and time to reach pseudo steady state) was observed in B1 (fresh NS) and B2 (recycled NS), probably due to the adequate time for MOs to uptake the nutrients.

CHAPTER 4 Biofiltration of methane and styrene mixtures

Avant propos:

L'article "Simultaneous biodegradation of methane and styrene in biofilters packed with inorganic supports: experimental and macrokinetic study" a été publié dans le journal "Chemosphere" Volume 252, August 2020, 126492.

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Titre: Biodégradation simultanée du méthane et du styrène dans des biofiltres sur des supports inorganiques: études expérimentale et macro-cinétique

Title: Simultaneous biodegradation of methane and styrene in biofilters packed with inorganic supports: experimental and macrokinetic study

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Contribution to the document: This paper is relevant to the third objective of the thesis. Four methane biofilters with similar packing materials and operating conditions were evaluated and compared in order to remove methane and styrene, two pollutants originated often from wastewater sources. Performance of methane biofilters in the absence and presence of styrene were compared and discussed.

Simultaneous biodegradation of methane and styrene in biofilters packed with inorganic supports: experimental and macrokinetic study

4.1 Résumé

Quatre biofiltres de 0.018 m^3 ont été opérés pendant 165 jours pour éliminer le méthane (CH_4), un gaz à effet de serre nocif, et le styrène (C_8H_8), un composé organique volatil cancérigène. La charge d'entrée (IL) de styrène a été maintenue constante dans chaque biofiltre. B-ME (IL de 0 $gC_8H_8.m^{-3}.h^{-1}$), B-200 (IL de 9 $gC_8H_8.m^{-3}.h^{-1}$), B-500 (IL de 22 $gC_8H_8.m^{-3}.h^{-1}$) et B-700 (IL de 32 $gC_8H_8.m^{-3}.h^{-1}$) ont été étudiés pour la biofiltration simultanée du CH_4 et du C_8H_8 en utilisant une teneur en CH_4 IL de 7 à 60 $gCH_4.m^{-3}.h^{-1}$. Des conversions de C_8H_8 de 64±1, 94±5, 100 et 100% ont été obtenues pour des ILs de 7, 20, 40 et 60 $gCH_4.m^{-3}.h^{-1}$, respectivement. En augmentant progressivement l'IL du C_8H_8 de 0 à 32 $gC_8H_8.m^{-3}.h^{-1}$, une conversion moyenne de CH_4 de 78±2, 74±4, 63±6 et 57±9% a été obtenue pour les biofiltres B-ME, B-200, B-500 et B-700, respectivement. Une étude macro-cinétique basée sur le modèle de Michaelis-Menten a montré qu'une inhibition non compétitive s'est produite lors de la biofiltration du CH_4 en présence de C_8H_8.

Mots-clés: Biofiltration, Méthane, Styrène, Inhibition, Mélange de polluants, Paramètres macro-cinétiques.

4.2 Abstract

Four 0.018 m^3 biofilters were operated for 165 days to eliminate methane (CH_4), a harmful greenhouse gas, and styrene (C_8H_8), a carcinogenic volatile organic compound. Styrene inlet load (IL) was kept constant in each biofilter. B-ME (IL of 0 $gC_8H_8.m^{-3}.h^{-1}$), B-200 (IL of 9 $gC_8H_8.m^{-3}.h^{-1}$), B-500 (IL of 22 $gC_8H_8.m^{-3}.h^{-1}$) and B-700 (IL of 32 $gC_8H_8.m^{-3}.h^{-1}$) at CH_4 IL rage of 7 to 60 $gCH_4.m^{-3}.h^{-1}$ were studied for simultaneous biofiltration of CH_4 and C_8H_8. Average C_8H_8 removal efficiencies (RE) of 64±1, 94±5, 100 and 100% were obtained at CH_4 ILs of 7, 20, 40 and 60 $gCH_4.m^{-3}.h^{-1}$, respectively. By increasing the C_8H_8 IL from 0 to 32 $gC_8H_8.m^{-3}.h^{-1}$, average CH_4 RE of 78±2, 74±4, 63±6 and 57±9% was obtained in B-ME, B-200, B-500 and B-700, respectively. A macrokinetic study based on the Michaelis-Menten model showed an uncompetitive inhibition during CH_4 biofiltration in presence of C_8H_8.

Keywords: Biofiltration, Methane, Styrene, Inhibition, Mixed pollutants, Macrokinetic parameters.

4.3 Introduction

Methane is emitted to the atmosphere from both natural and anthropogenic sources. Among anthropogenic sources, after carbon dioxide (CO_2), CH_4 is the second greatest contributor to global warming [234]. The global warming potential (GWP) of CH_4 is 25 over a 100-year time frame [235]. It is reported that 8 Gigatons of CH_4 are emitted from anthropogenic sources, on a CO_2 equivalent basis, annually worldwide [236]. The contribution of agricultural industry and waste sectors, i.e. municipal solid waste management, wastewater treatment plants (WWTPs) and landfills, as well as livestock, in CH_4 emission is forecasted to increase in the coming decades, since food production and waste management will rise with population growth [18, 234, 237, 238]. Approaches based on chemical oxidation are not reasonable for mitigating CH_4 at concentrations lower than 5% (v/v), while biological techniques, such as biofiltration, are shown to be promising [124, 213].

One of the challenges in CH_4 biofiltration is the accompaniment of non-methane organic compounds (NMOCs) in polluted air, which may negatively affect the performance of a CH_4 biofilter [21, 239]. These NMOCs mainly consist of alkanes, alkenes, oxygenated compounds (ketones, alcohols, aldehydes and acids), sulfur compounds, chlorinated compounds and aromatics, such as benzene (C_6H_6), toluene (C_7H_8), xylene (C_8H_{10}) and styrene (C_8H_8) [22, 240]. Waste sectors, such as WWTPs and municipal solid waste landfills, and also energy sectors, such as refineries and petrochemical complexes, produce waste gases including CH_4 and C_8H_8 [17, 241]. Styrene has extreme harmful effects on human health, when released to the atmosphere. The International Agency for Research on Cancer (IARC) has announced that C_8H_8 is a carcinogen compound in long-term exposure [24]. Hence, few researchers investigated on C_8H_8 elimination by means of biofilters and it was proved that methanotrophic microorganisms (MOs) are well capable of biodegrading C_8H_8 [29, 242-246]. However, there might be interactions between C_8H_8 and CH_4 during bio-oxidation when they are biofiltered as a mixture. A competition might take place between CH_4 and C_8H_8 for bonding with MOs, which could end up with a decrease/increase in removal efficiency (RE) of CH_4 and/or C_8H_8. An inhibition effect might happen when biodegradation of one component stops the interaction of the other component with MOs and hinders bio-oxidation. Therefore, the simultaneous biofiltration of

C_8H_8 and CH_4 might cause an inhibitory effect in the biofilter and total RE could be effected negatively.

The mixtures of CH_4 and some NMOCs (such as trichloroethylene, ethanol, methanol, benzene and ethylene) were targeted for removal in biofilters [218, 247-249]. However, to our knowledge, elimination of CH_4 and C_8H_8 mixtures in a biofilter has not been investigated.

This study examines the performance of inorganic packed bed biofilters for treating CH_4 and C_8H_8, in order to study the biodegradation of the mixture. For demonstrating the inhibitory effect most likely caused by C_8H_8 during CH_4 biodegradation, CH_4 biofilter was studied individually and in presence of different concentrations of C_8H_8. Effects of CH_4 and C_8H_8 inlet concentrations on the biofilters' performance were evaluated. Finally, a macrokinetic study was used to reach a better understanding of the biofilters' behavior as a function of CH_4 and C_8H_8 inlet and outlet concentrations.

4.4 Materials and methods

4.4.1 Lab-scale biofilter set-up

Four 0.018 m^3 Plexiglas lab-scale up-flow biofilters with a height of 1 m and a diameter of 0.15 m were used for 165 days. B-ME was used for treating CH_4 and 3 other biofilters B-200, B-500 and B-700 were used for treating the mixtures of CH_4 and C_8H_8. Each biofilter included 3 beds of 0.30 m height and 4 ports were considered in order to measure the gases' concentrations. A schematic flow chart of the biofilter is shown in Figure 4.1.

Since the gas is injected from bottom of the biofilter, the bottom bed is more exposed to pressure drop and clogging issues [223]. Therefore, in all four (4) biofilters, in order to avoid clogging problems, the bottom beds were filled with inorganic materials (stone-based) with an average diameter of 7.5 mm (void fraction of 0.55, water holding capacity of 0.15, density of 750 kg m^{-3} and specific surface area of 470 m^2 m^{-3}). The middle and top beds were filled with a different inorganic material (stone-based) with a smaller average diameter of 5.0 mm (void fraction of 0.43, water holding capacity of 0.07, density of 1200 kg m^{-3} and specific surface area of 1250 m^2 m^{-3}). For confidential reasons, the name of the packings cannot be revealed. A mixture of humidified air, CH_4 (Praxair Inc., Canada) or/and C_8H_8 ($\geq$ 99%, Sigma-Aldrich, USA) represented the contaminated air. Dry air was humidified by passing through a bubbler

humidifier with a diameter of 0.10 m and height of 0.75 m. Styrene was also added to the system by passing dry air into a C_8H_8 bubbler with a volume of 5×10^{-4} m^3. Flow rates of CH_4 and C_8H_8 were adjusted by mass flow controllers (Brooks, USA). Dry air flow rates were regulated by volumetric flow meters (Brooks, USA).

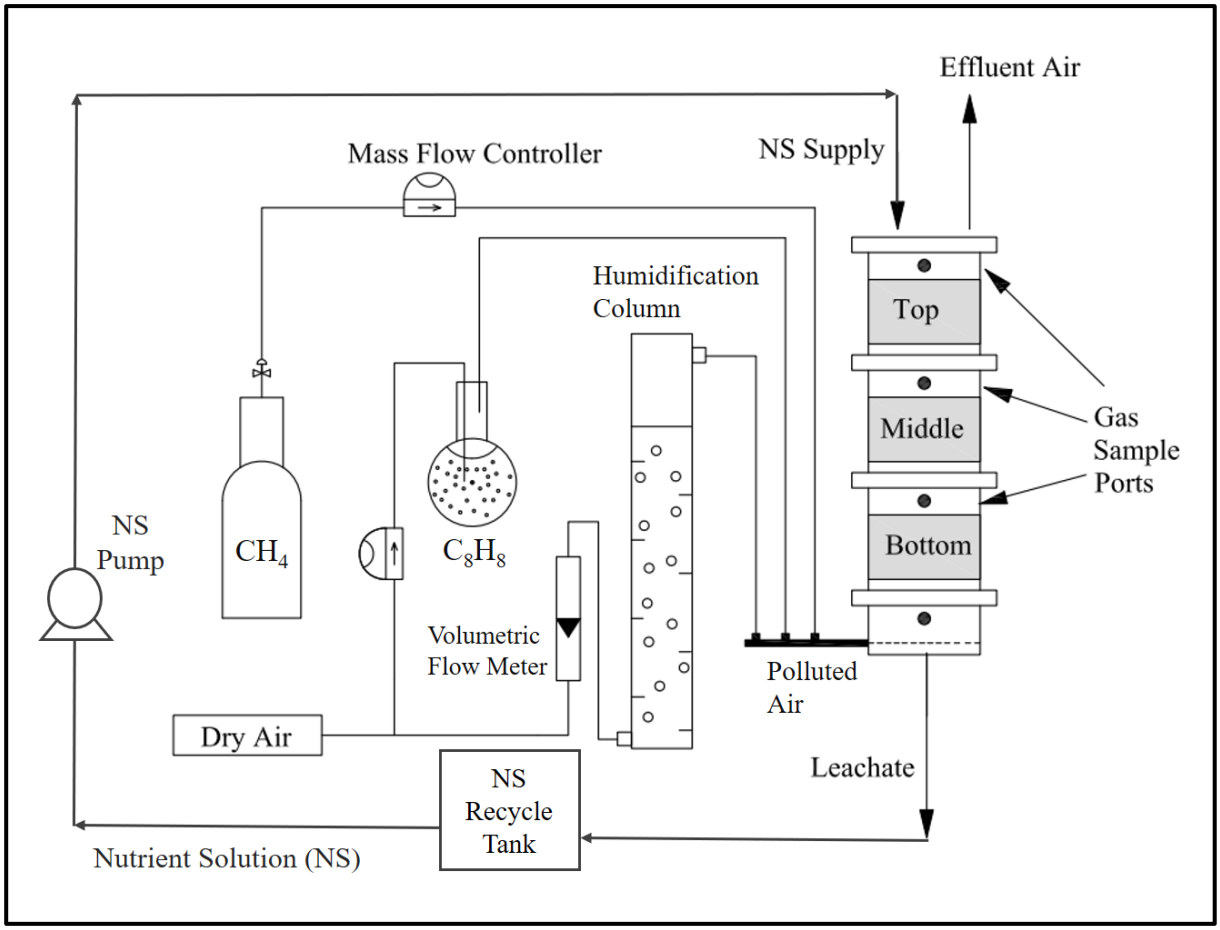

Figure 4.1: Schematic of the lab-scale biofilters

4.4.2 Analytical tools

Methane concentration in gas phase was measured by a total hydrocarbon analyzer equipped with a continuous flame ionization detector (FIA 510, Horiba, Japan) with a minimum detection limit of 0.5 ppmv (3.3×10^{-4} $g_{CH4}.m^{-3}$). The hydrocarbon analyzer was calibrated prior to measuring. Filter bed's pressure drop was measured by means of a differential manometer (Type 4, Air Flow Developments, UK) with a detection limit of 0.01 $cmH_2O.m^{-1}$.

4.4.3 Biofilter performance parameters

Performance of each biofilter was evaluated by means of the following equations:

IL_i: inlet load of pollutant i ($g.m^{-3}.h^{-1}$)

$$IL_i = \frac{C_{i,in}}{EBRT} \quad (1)$$

RE_i: removal efficiency of pollutant i (%)

$$RE_i = \frac{C_{i,in} - C_{i,out}}{C_{i,in}} \times 100 \quad (2)$$

EC_i: elimination capacity of pollutant i ($g.m^{-3}.h^{-1}$)

$$EC_i = IL_i \times RE_i \quad (3)$$

Empty Bed Residence Time (h)

$$EBRT = \frac{V}{Q} \quad (4)$$

Where $C_{i,in}$ and $C_{i,out}$ are the pollutant inlet and outlet concentrations ($g.m^{-3}$), respectively, which could be either CH_4 or C_8H_8. Q is the total gas flow rate in $m^3.h^{-1}$ and V is the biofilter's volume in m^3.

4.4.4 Experimental methods and operating conditions

The packing materials were washed and cleaned by tap water and embedded in filter beds. Afterward, 5×10^{-3} m^3 of leachate from an active CH_4 biofilter (IL=63 $g.m^{-3}.h^{-1}$, RE≈60%) was used to inoculate the 4 biofilters. The leachate was added to each biofilter from the top and recycled 4 times. Air flow rate was fixed at 0.18 $m^3.h^{-1}$ and empty bed residence time (EBRT) was 0.1 h for all 4 biofilters.

Two acclimation periods were considered in the present study. During the first acclimation period, a mixture of CH_4 and humid air was passing through the 4 biofilters for 15 days at CH_4 IL of 7 $g.m^{-3}.h^{-1}$. In the second acclimation period, in addition to 7 $g.m^{-3}.h^{-1}$ of CH_4, C_8H_8 ILs varying from 9 to 32 $g.m^{-3}.h^{-1}$ were injected to B-200, B-500 and B-700. B-ME was left to continue without any C_8H_8 addition at the same CH_4 IL.

Operating Conditions		Phase 0	Phase 1	Phase 2	Phase 3	Phase 4	Phase 5	Phase 6
		15 days	30 days	30 days	30 days	30 days	15 days	30 days
		(No C_8H_8)	(day 1 to 30)[1]	(day 31 to 60)	(day 61 to 90)	(day 91 to 120)	(day 121 to 135)[4]	(day 136 to 165)
		Acclimation I[2]	Acclimation II[3]			Shutdown		
Biofilters	$IL_{C_8H_8}$ ($g.m^{-3}.h^{-1}$)	IL_{CH_4} ($g.m^{-3}.h^{-1}$)						
B-ME	0	7	7	20	40	0	60	60
B-200	9	7	7	20	40	0	60	60
B-500	22	7	7	20	40	0	60	60
B-700	32	7	7	20	40	0	60	60

1 Beginning of phase 1 was considered as the first operating day, when C_8H_8 was injected to the biofilters.
2 Acclimation I was done in presence of only CH_4 as the single pollutant during 15 days in phase 0.
3 Acclimation II was done in presence of CH_4 and C_8H_8 as the mixed pollutants during 30 days in phase 1.
4 Phase 5 was considered as a 15-day recovery after a 30-day shutdown.

Table 4.1: Operating conditions

The second acclimation period lasted for 30 days. The experiments were divided into 6 phases as shown in Table 4.1 and simultaneous biofiltration of CH_4 and C_8H_8 were investigated. The phases were based on CH_4 and C_8H_8 inlet concentration variations and time. Experiments were conducted at CH_4 concentrations of 1000, 3000, 6000 and 9000 ppmv, corresponding to CH_4 ILs of 7, 20, 40 and 60 $g.m^{-3}.h^{-1}$.

In B-200, B-500 and B-700, which treated a mixture of CH_4 and C_8H_8, the C_8H_8 ILs were kept constant at 9, 22 and 32 $g.m^{-3}.h^{-1}$, respectively, corresponding to 200, 500 and 700 ppmv, respectively, while CH_4 ILs were varying regarding the phases. All the 4 biofilters were fed by 10^{-3} m^3 of nutrient solution (NS) per day from a 20×10^{-3} m^3 recycle tank with a liquid flow rate of 60×10^{-3} $m^3.h^{-1}$. The promising efficiency of recycling NS has been already demonstrated and the characteristics of the NS were described in a previous work [135]. The NS in the recycle tanks were refreshed at the beginning of each phase.

4.4.5 Macrokinetic study in CH_4+C_8H_8 biofiltration

Michaelis–Menten model was used to describe EC of a single pollutant in a biofilter [250, 251]:

$$EC_{CH_4} = \frac{EC_{CH_4,max} \times C_{ln,CH_4}}{K_S + C_{ln,CH_4}} \qquad (5)$$

Where $EC_{CH4,max}$ is the maximal EC of CH_4 ($g.m^{-3}.h^{-1}$), K_S is the macrokinetic saturation constant ($g.m^{-3}$) and $C_{ln,CH4}$ is the logarithmic average of the inlet and outlet concentrations of CH_4 ($g.m^{-3}$). Logarithmic average was shown to be a better representative of CH_4 concentration in a biofilter in comparison with arithmetic average [252]. In case of adding a second pollutant (C_8H_8), which could act as an inhibitor in CH_4 biofiltration, other terms have to be considered in equation 5. In order to reach a macrokinetic approach, the biological interactions between CH_4 (S), C_8H_8 (I) and MO were schematized in Figure 4.2, based on previous works on bio-kinetics [21, 253]. Intermediate complexes such as CH_4-MO (MOS), C_8H_8-MO (MOI) and CH_4-MO-C_8H_8 (MOSI) were considered during CH_4+C_8H_8 biodegradation. As illustrated in Figure 4.2, C_8H_8 might enter to a biological reaction with either MO or the intermediate complexes. Thus, macrokinetic inhibition constant K_I ($g.m^{-3}$) and average of inlet and outlet C_8H_8 concentrations $C_{ave,C8H8}$ ($g.m^{-3}$) were used to represent the interactions caused by C_8H_8 and

quantify the inhibition effect in the Michaelis–Menten single pollutant model [21, 208]. Following equations (6-9) quantify the 4 different inhibition types: competitive, uncompetitive, non-competitive and mixed inhibition. The difference between them is lied in the way in which CH_4, C_8H_8 and MO are interacting together as illustrated in Figure 4.2.

$$\begin{array}{ccccc} \mathrm{MO} & + \mathrm{S} & \rightleftarrows & MOS & \rightarrow \quad C + B + \mathrm{MO} \\ + & & & + & \\ \mathrm{I} & & & \mathrm{I} & \\ \uparrow\downarrow & & & \uparrow\downarrow & \\ \mathrm{MOI} & + \mathrm{S} & \rightleftarrows & \mathrm{MOSI} & \end{array}$$

Figure 4.2: Schematic of interactions between CH_4, C_8H_8 and MO. S as substrate (CH_4), I as inhibitor (C_8H_8), C and B as products (CO_2 and biomass, respectively). MOS, MOI and MOSI as intermediate complexes during biofiltration of CH_4.

Competitive inhibition: C_8H_8 (I) interacts with MO, producing MO-C_8H_8 (MOS) complex, and prevent CH_4 (S) from bonding to MO. Therefore, C_8H_8 (I) and CH_4 (S) are in a competition for interacting with MO [21, 253].

$$\mathrm{EC}_{\mathrm{CH_4}} = \frac{\mathrm{EC}_{\mathrm{CH_4,max}} \times \mathrm{C}_{\mathrm{ln,CH_4}}}{\mathrm{K_S}\left(1 + \frac{\mathrm{C}_{\mathrm{ave,C_8H_8}}}{\mathrm{K_I}}\right) + \mathrm{C}_{\mathrm{ln,CH_4}}} \qquad (6)$$

Uncompetitive inhibition: C_8H_8 (I) interacts with the intermediate formed from MO and CH_4 (MO-CH_4 complex (MOS)), producing an inactive intermediate complex (C_8H_8-MO-CH_4(MOSI)) [21, 253].

$$\mathrm{EC}_{\mathrm{CH_4}} = \frac{\mathrm{EC}_{\mathrm{CH_4,max}} \times \mathrm{C}_{\mathrm{ln,CH_4}}}{\mathrm{K_S} + \mathrm{C}_{\mathrm{ln,CH_4}}\left(1 + \frac{\mathrm{C}_{\mathrm{ave,C_8H_8}}}{\mathrm{K_I}}\right)} \qquad (7)$$

Non-competitive inhibition: C_8H_8 (I) interacts with both MO and MO-CH_4 (MOS) complex [21, 253].

$$EC_{CH_4} = \frac{\frac{EC_{CH_4,max} \times C_{ln,CH_4}}{\left(1 + \frac{C_{ave,C_8H_8}}{K_I}\right)}}{K_S + C_{ln,CH_4}} \quad (8)$$

Mixed inhibition: CH_4 (S) interacts with MO-C_8H_8 (MOI) complex and produces the inactive complex of C_8H_8-MO-CH_4 (MOSI) [21, 253].

$$EC_{CH_4} = \frac{EC_{CH_4,max} \times C_{ln,CH_4}}{K_S + C_{ln,CH_4} + \frac{C_{ln,CH_4}^2}{K_I}} \quad (9)$$

4.5 Results and discussion

4.5.1 Effect of CH_4 concentration on C_8H_8 biofiltration

Figure 4.3 presents the C_8H_8 RE in the 4 biofilters as a function of CH_4 IL. The values presented in the following sections are the RE values when the biofilters were in pseudo steady state. At low CH_4 IL of 7 $gCH_4.m^{-3}.h^{-1}$, C_8H_8 RE reached 62, 65 and 64% for C_8H_8 ILs of 9, 22, 32 $gC_8H_8.m^{-3}.h^{-1}$, respectively. At CH_4 IL of 20 $gCH_4.m^{-3}.h^{-1}$ (day 31 to 60), C_8H_8 RE reached 100, 88 and 93% for C_8H_8 ILs of 9, 22, 32 $gC_8H_8.m^{-3}.h^{-1}$, respectively. At high CH_4 ILs of 40 and 60 $gCH_4.m^{-3}.h^{-1}$, C_8H_8 RE of 100% was observed for C_8H_8 ILs from 9 to 32 $gC_8H_8.m^{-3}.h^{-1}$ (day 61 to 165).

Average C_8H_8 RE of 64±1% was observed at CH_4 IL of 7 $gCH_4.m^{-3}.h^{-1}$. For CH_4 ILs from 20 to 60 $gCH_4.m^{-3}.h^{-1}$, no significant difference was observed in C_8H_8 RE as a function of CH_4 IL, which was 94±5% at 20 $gCH_4.m^{-3}.h^{-1}$ and 100% at both 40 and 60 $gCH_4.m^{-3}.h^{-1}$. The high EBRT of 0.1 h (6 min) could explain the C_8H_8 RE of 100%. An EBRT of 0.0333 h (2 min) was reported to be adequate for complete removal of C_8H_8 in an inorganic biofilter at C_8H_8 ILs up to 150 $gC_8H_8.m^{-3}.h^{-1}$ [27]. Even for lower EBRT of 0.0125 h (45 s), Pérez *et al*. [28] reported a C_8H_8 RE of 95% in an organic biofilter for a C_8H_8 IL of 22 $gC_8H_8.m^{-3}.h^{-1}$. Rene *et al*. [254] attributed the high C_8H_8 RE in biofilters to the presence of fungi as the potential bio-oxidizer.

Kennes *et al*. [255] also showed that the presence of fungi in filter beds leads to high RE for hydrophobic VOCs, such as C_8H_8.

Figure 4.3 also indicates the RE of C_8H_8 for each bed of the biofilters (bottom, middle and top beds, respectively). At CH_4 IL of 7 $gCH_4.m^{-3}.h^{-1}$, when C_8H_8 IL increased from 9 to 32 $gC_8H_8.m^{-3}.h^{-1}$, C_8H_8 RE declined in the bottom beds from 36 to 29% and enhanced in the top bed from 7 to 14%. No clear trend was observed in the middle bed with C_8H_8 RE of 19, 25 and 21 obtained at C_8H_8 IL of 9, 22 and 32 $gC_8H_8.m^{-3}.h^{-1}$, respectively.

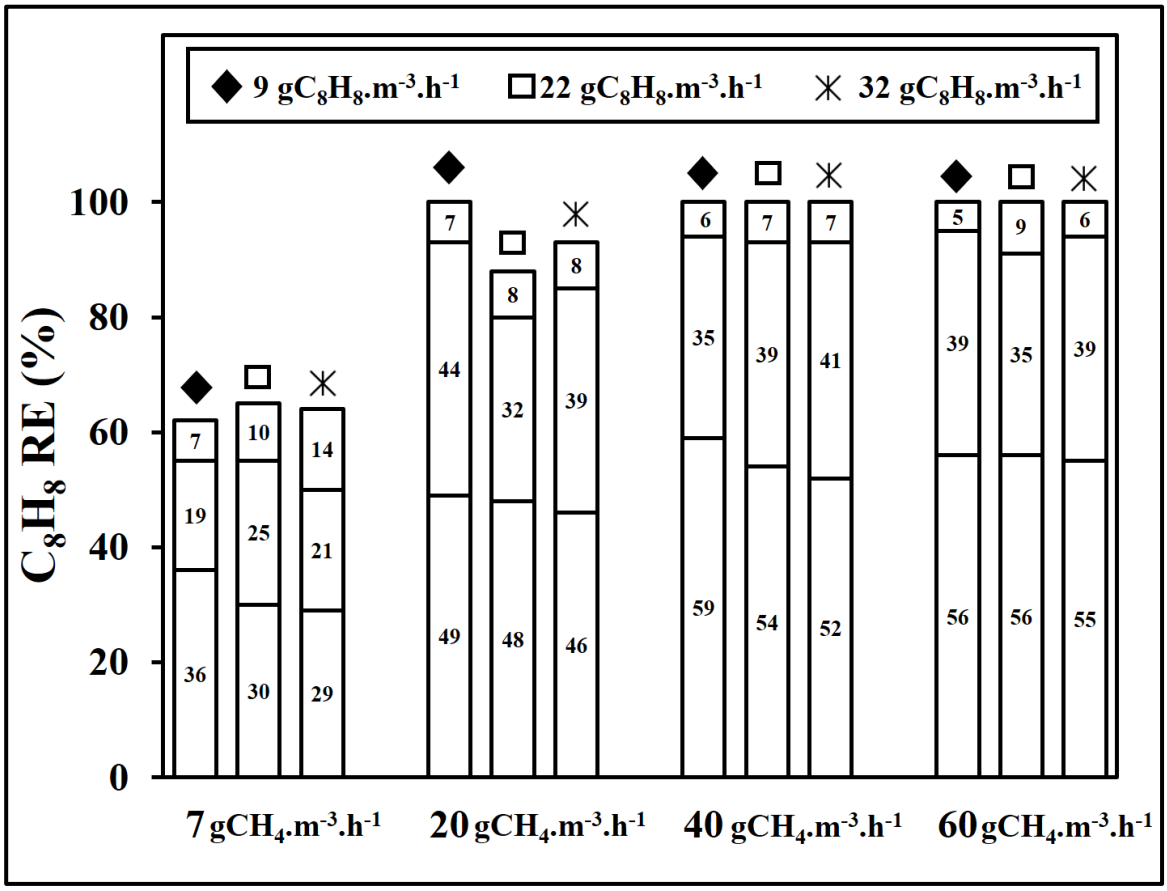

Figure 4.3: Removal efficiency of C_8H_8 as a function of CH_4 inlet load

For all 4 biofilters, the biggest portions of C_8H_8 were eliminated in the 2 first beds (bottom and middle beds) of the biofilters. For CH_4 ILs from 20 to 60 $gCH_4.m^{-3}.h^{-1}$, 91±5% of C_8H_8 was removed in the bottom and middle beds and 7±1% of C_8H_8 was treated in the top beds. The same result was observed by Rene *et al*. [256] when treating a mixture of C_8H_8 and acetone

(C_3H_6O). It was shown that in an inorganic biofilter at a C_8H_8 IL of 214 $gC_8H_8.m^{-3}.h^{-1}$ (EBRT of 17.1 s), 74% of C_8H_8 was removed in the first half of the biofilter.

For the whole CH_4 ILs tested, slight declines in C_8H_8 RE were observed in the bottom beds from 49 to 46% (CH_4 IL of 20 $gCH_4.m^{-3}.h^{-1}$), 59 to 52% (CH_4 IL of 40 $gCH_4.m^{-3}.h^{-1}$) and 56 to 55% (CH_4 IL of 60 $gCH_4.m^{-3}.h^{-1}$) when C_8H_8 IL increased from 9 to 32 $gC_8H_8.m^{-3}.h^{-1}$. This RE reduction was indicative of an ascending kinetic limitation and partial inhibition due to excess bioavailability of C_8H_8 in the biofilm [156]. For the same CH_4 ILs, no specific tendency in C_8H_8 RE was observed in the middle and top beds as a function of C_8H_8 ILs.

4.5.2 Effect of C_8H_8 concentration on CH_4 biofiltration

Figure 4.4 illustrates the CH_4 RE for each bed (bottom, middle and top beds) as a function of C_8H_8 IL. In terms of changes in CH_4 removal in each biofilter as a function of CH_4 IL, CH_4 RE in B-ME, B-200, B-500 and B-700 decreased from 80 to 76, 78 to 69, 70 to 54, 68 to 43%, respectively, by increasing CH_4 IL from 7 to 60 $gCH_4.m^{-3}.h^{-1}$ and by increasing C_8H_8 IL from 0 to 32 $gC_8H_8.m^{-3}.h^{-1}$. This RE decline showed a shift from a mass transfer regime to a kinetic limited regime in all 4 biofilters by the increase of CH_4 IL. For lower ILs (7 and 20 $gCH_4.m^{-3}.h^{-1}$), biofilters' performance was controlled by mass transfer, because of the low bioavailability of CH_4 in biofilm. In contrast, for higher ILs (40 and 60 $gCH_4.m^{-3}.h^{-1}$), RE was kinetically controlled due to excess CH_4 available for MOs, which influenced biofilters' performance negatively by inhibiting MOs from biodegrading CH_4 [225].

Regarding the effect of C_8H_8 on behavior of biofilters in CH_4 removal, a declining trend in CH_4 RE was observed by ascending C_8H_8 IL. The average CH_4 RE decreased from 78±2 to 57±9% when C_8H_8 IL increased from 0 to 32 $gC_8H_8.m^{-3}.h^{-1}$, which showed that CH_4 biodegradation was inhibited due to the presence of C_8H_8.

In B-ME, for all tested CH_4 ILs, the bottom bed contributed the most to CH_4 removal with CH_4 RE of 33, 30, 28 and 33% and the top bed contributed the least by 16, 19, 22 and 19% at CH_4 IL of 7, 20, 40 and 60 $gCH_4.m^{-3}.h^{-1}$, respectively. While in biofilters treating a mixture of CH_4 and C_8H_8, at the same CH_4 IL of 7, 20, 40 and 60 $gCH_4.m^{-3}.h^{-1}$, the top bed removed the biggest portion of CH_4. In B-200, CH_4 RE of 30, 29, 27 and 24% were observed in the top bed, while 20, 22, 21 and 24% were obtained in the bottom bed for CH_4 IL of 7, 20, 40 and 60 $gCH_4.m^{-3}.h^{-1}$,

respectively. At same CH_4 ILs in B-500, CH_4 RE of 25, 26, 22 and 22% were reached in the top bed and in the bottom bed, 19, 20, 19 and 14% were observed. In the top bed of B-700, CH_4 RE were 25, 23, 22 and 17%, while 18, 21, 16 and 14% were reached in the bottom bed.

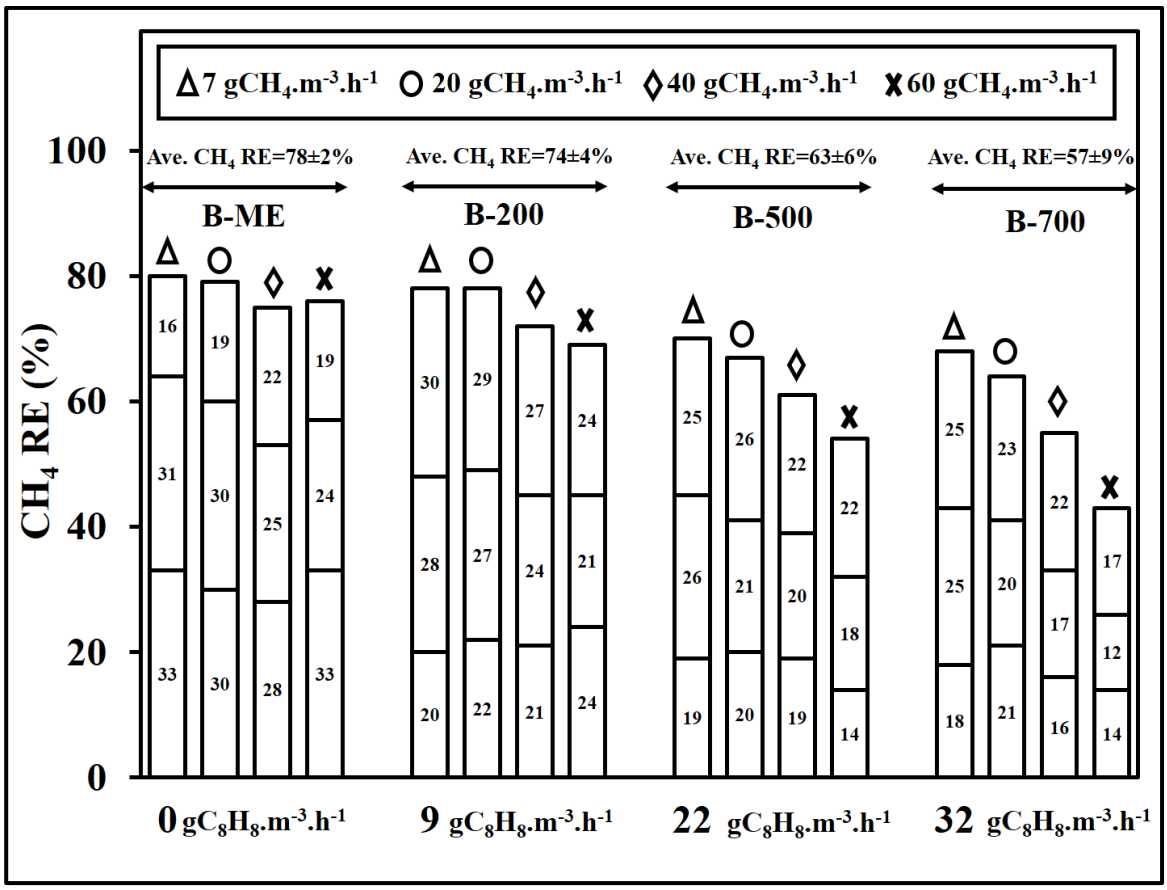

Figure 4.4: Removal efficiency of CH_4 as a function of C_8H_8 inlet load

From bottom to the top, the declining trend of CH_4 RE in B-ME and the ascending trend of CH_4 RE in B-200, B-500 and B-700 pronounced the inhibitory effect of C_8H_8 on the biofilters' behavior. The general decreasing trend of CH_4 RE from bottom to the top in single pollutant up-flow biofilters (i.e. CH_4 biofilters) had been shown in previous studies [222, 257]. Nevertheless, the ascending tendencies of CH_4 RE through the beds in B-200, B-500 and B-700 were related to the declining trends of C_8H_8 RE from bottom to the top of the biofilters. Since more than 90% of the C_8H_8 was degraded in bottom and middle beds in B-200, B-500 and B-700, no significant inhibition of MOs for CH_4 biodegradation showed up in top beds. Therefore, the highest CH_4 RE were obtained in top beds for biofilters treating CH_4 and C_8H_8, simultaneously.

The MOs' co-metabolism capability resulted in simultaneous degradation of CH_4 and C_8H_8. However, C_8H_8 is more degradable than CH_4 because of its higher solubility in the biofilm, which could be revealed by Henry's constant of 0.3 for C_8H_8 and 30 for CH_4 at 293 K. Since C_8H_8 biodegradation takes place first, vinylphenols and vinylcatechols may have formed as by-products in bottom beds [258]. Phenolic and catecholic compounds were shown to have inhibitory effects on CH_4 biofiltration [259].

To our best knowledge, biofiltration of CH_4 and C_8H_8, as a mixture, has not been reported in literature. However, CH_4 removal in presence of other aromatics such as C_6H_6 and C_7H_8 was studied in biofilters, bio-covers, batch bioreactors, bio-membranes and bio-scrubbers. Scheutz *et al*. [247] reported no effect of C_6H_6 (0.03 $gC_6H_6.m^{-3}.h^{-1}$) and C_7H_8 (0.01 $gC_7H_8.m^{-3}.h^{-1}$) on biofiltration of CH_4 (7.7 $gCH_4.m^{-3}.h^{-1}$) with CH_4 RE of 77% (CH_4 EC of 5.8 $gCH_4.m^{-3}.h^{-1}$) by means of batch experiments. This neutral effect might have been due to the high ratio of CH_4 IL to C_6H_6+C_7H_8 IL, which is 193 $gCH_4.g(C_6H_6+C_7H_8)^{-1}$. In the present study, the highest CH_4 IL to C_8H_8 IL was 7 $gCH_4.gC_8H_8^{-1}$, which is similar to real emission sources of mixed CH_4 and C_8H_8 [25, 260]. In the current study, as shown in Figure 4.4, a 21% reduction in CH_4 RE occurred by increasing C_8H_8 IL from 0 to 32 $gC_8H_8.m^{-3}.h^{-1}$, corresponding to the C_8H_8 concentration of 0 to 3.2 $gC_8H_8.m^{-3}$. In batch reactor study, Chiemchaisri *et al*. [248] showed a toxic effect of C_6H_6 (C_6H_6 IL $\geq$ 0.04 $gC_6H_6.m^{-3}$) on CH_4 RE at CH_4 inlet concentration of 24.2 $gCH_4.m^{-3}$ (a 10% reduction in CH_4 RE). The negative effect was justified by inhibitory potency of aromatic compounds [21, 261, 262].

4.5.3 Elimination capacities of biofilters

Figure 4.5 shows the total and individual ECs of CH_4 and C_8H_8 as well as ILs for the 4 biofilters. Total EC refers to the sum of CH_4 and C_8H_8 EC. Likewise, total IL refers to the sum of CH_4 and C_8H_8 IL. The values of ECs presented in Figure 4.5 are the ECs when the biofilters were in pseudo steady state at the end of each operating phase (days 30, 60, 90 and 165). For the mixed pollutant biofilters, different ECs were obtained due to different contribution of each pollutant in the total IL. The highest CH_4 EC (45 $gCH_4.m^{-3}.h^{-1}$) was obtained in B-ME in the absence of C_8H_8 (CH_4 IL of 60 $gCH_4.m^{-3}.h^{-1}$), while the maximum CH_4 EC declined to 41, 32 and 26

$gCH_4.m^{-3}.h^{-1}$ in B-200, B-500 and B-700, respectively, since C_8H_8 contribution in total IL increased from 9 to 32 $gC_8H_8.m^{-3}.h^{-1}$.

In B-ME (Figure 4.5a), with no C_8H_8, when CH_4 IL increased from 7 to 60 $gCH_4.m^{-3}.h^{-1}$, CH_4 EC increased from 5 to a maximum value of 45 $gCH_4.m^{-3}.h^{-1}$. Figure 4.5b shows that in B-200 with increasing total IL from 16 to 69 $g(CH_4+C_8H_8).m^{-3}.h^{-1}$, total EC increased from 11 to 50 $g(CH_4+C_8H_8).m^{-3}.h^{-1}$. At a C_8H_8 IL of 9 $gC_8H_8.m^{-3}.h^{-1}$ in B-200, C_8H_8 EC was 6 $gC_8H_8.m^{-3}.h^{-1}$ after 30 days and reached a complete EC at day 60 (9 $gC_8H_8.m^{-3}.h^{-1}$, C_8H_8 RE=100%) and stayed unchanged until day 165, while CH_4 EC increased from 5 to 41 $gCH_4.m^{-3}.h^{-1}$ at a CH_4 IL range of 7 to 60 $gCH_4.m^{-3}.h^{-1}$.

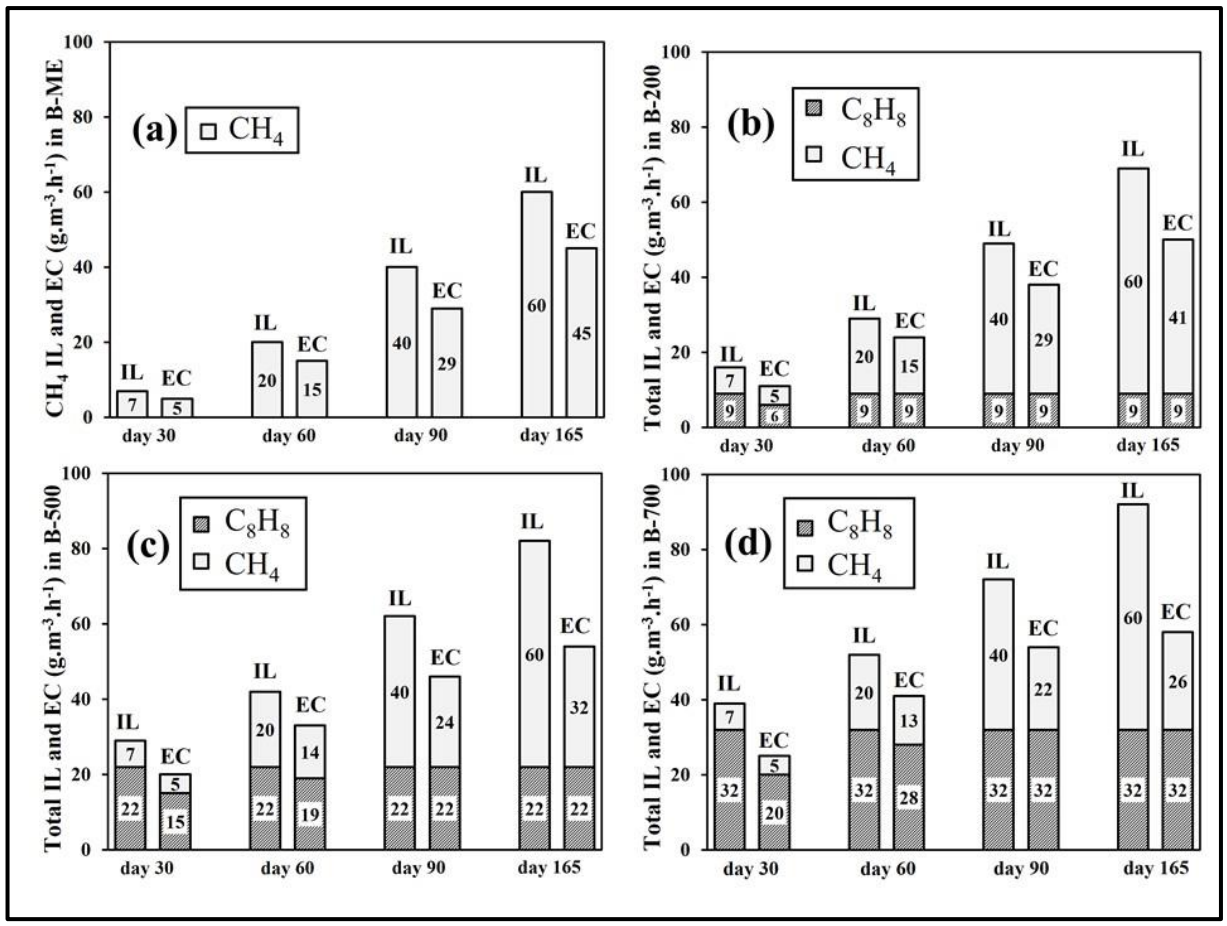

Figure 4.5: Elimination capacities and inlet loads of CH_4 and C_8H_8 as a function of time

In B-500, as shown in Figure 4.5c, at a C_8H_8 IL of 22 $gC_8H_8.m^{-3}.h^{-1}$, C_8H_8 EC was 15 $gC_8H_8.m^{-3}.h^{-1}$ after 30 days and 19 $gC_8H_8.m^{-3}.h^{-1}$ after 60 days and finally, reached a

complete EC (C_8H_8 EC=22 $gC_8H_8.m^{-3}.h^{-1}$; C_8H_8 RE=100%) at day 90 and maintained constant until day 165. Meanwhile, at a CH_4 IL range of 7 to 60 $gCH_4.m^{-3}.h^{-1}$, CH_4 EC increased from 5 to 32 $gCH_4.m^{-3}.h^{-1}$.

As shown in Figure 4.5d, at C_8H_8 IL of 32 $gC_8H_8.m^{-3}.h^{-1}$, C_8H_8 EC was 20 $gC_8H_8.m^{-3}.h^{-1}$ after 30 days and 28 $gC_8H_8.m^{-3}.h^{-1}$ after 60 days in B-700. At day 90, B-700 reached a complete EC of 32 $gC_8H_8.m^{-3}.h^{-1}$ (C_8H_8 RE=100%) and continued to work steadily, concerning complete C_8H_8 removal, until day 165. The complete C_8H_8 elimination was reached later in B-700 and B-500 compared to B-200, which could be explained by higher C_8H_8 IL which could lead to a partial inhibition of MOs in the biofilter [251]. When CH_4 IL varied from 7 to 60 $gCH_4.m^{-3}.h^{-1}$ in B-700, CH_4 EC increased from 5 to 26 $gCH_4.m^{-3}.h^{-1}$. Kim *et al*. [239] observed a CH_4 EC increase from 20 to 72 $gCH_4.m^{-3}.h^{-1}$ corresponding to a CH_4 IL range from 27 to 99 $gCH_4.m^{-3}.h^{-1}$ in a mixed organic and inorganic packed biofilter treating a mixture of CH_4, C_7H_8 (IL of 1.19 $gC_7H_8.m^{-3}.h^{-1}$) and C_6H_6 (IL of 0.46 $gC_6H_6.m^{-3}.h^{-1}$).

Figure 4.5 shows that at CH_4 IL of 7 $gCH_4.m^{-3}.h^{-1}$, CH_4 EC in all 4 biofilters maintained constant at 5 $gCH_4.m^{-3}.h^{-1}$, despite C_8H_8 IL increased from 0 to 32 $gC_8H_8.m^{-3}.h^{-1}$. The biofilters' behavior was almost the same at CH_4 IL of 20 $gCH_4.m^{-3}.h^{-1}$ and no significant change in CH_4 EC was observed for 4 biofilters and CH_4 EC reached 15, 15, 14 and 13 $gCH_4.m^{-3}.h^{-1}$ at C_8H_8 ILs of 0, 9, 22 and 32 $gC_8H_8.m^{-3}.h^{-1}$, respectively. This agrees with observations of Scheutz *et al*. [247] discussed above, which pronounced a neutral effect of low ILs of C_6H_6 (0.03 $gC_6H_6.m^{-3}.h^{-1}$) and C_7H_8 (0.01 $gC_7H_8.m^{-3}.h^{-1}$) on CH_4 biofiltration.

At CH_4 IL of 40 $gCH_4.m^{-3}.h^{-1}$, CH_4 ECs slightly decreased by increasing C_8H_8 IL and CH_4 ECs of 29, 29, 24 and 22 $gCH_4.m^{-3}.h^{-1}$ were observed (24% reduction) at C_8H_8 ILs of 0, 9, 22 and 32 $gC_8H_8.m^{-3}.h^{-1}$, respectively. This declining tendency was clear at CH_4 IL of 60 $gCH_4.m^{-3}.h^{-1}$, when at C_8H_8 ILs of 0, 9, 22 and 32 $gC_8H_8.m^{-3}.h^{-1}$, CH_4 ECs of 45, 41, 32 and 26 $gCH_4.m^{-3}.h^{-1}$ (42% reduction) were obtained. The drop in CH_4 EC could be explained by the interactions between two pollutants, which made it more difficult for CH_4 (substrate) to reach MOs when C_8H_8 (co-substrate) IL is high [263]. Besides, increasing the total IL from 7 to 92 $g(CH_4+C_8H_8).m^{-3}.h^{-1}$ could increase the biofilm thickness and biomass accumulation, which could limit the mass transfer of CH_4 from gas phase to biofilm (diffusion limitation) [225] and caused lower CH_4 EC in B-700 (26 $gCH_4.m^{-3}.h^{-1}$) compared to B-500 (32 $gCH_4.m^{-3}.h^{-1}$), for instance. Elevated pressure drop represents the growth of biofilm thickness [196, 264]. Pressure

drop was 0.01 $cmH_2O.m^{-1}$ at day 1 and increased to 0.07, 0.43, 1.28 and 1.68 $cmH_2O.m^{-1}$ in biofilters B-ME, B-200, B-500 and B-700, respectively, at the end of the experiments (day 165). This is in agreement with results obtained by Ménard *et al*. [217], where an inorganic packed bed biofilter with an EBRT of 0.07 h (4.2 min) was used to treat a mixture of CH_4 and C_7H_8. At constant CH_4 IL of 66 $gCH_4.m^{-3}h^{-1}$, CH_4 EC decreased from 18 to 2 $gCH_4.m^{-3}h^{-1}$ (90% reduction) with increasing C_7H_8 IL from 0 to 46 $gC_7H_8.m^{-3}h^{-1}$ and pressure drop increased to a maximum of 3.95 $cmH_2O.m^{-1}$. The higher pressure drop (57%) and the higher CH_4 EC reduction (53%) reported by Ménard et al. [217] compared to the present study are related to several factors, such as the microbial communities, packing materials and biofilter configuration [197, 222-224, 239, 265-268].

4.5.4 Determination of macrokinetic parameters

In order to obtain the best estimation of kinetic parameters ($EC_{CH4,max}$, K_S and K_I), nonlinear equations 5-9 were used for data fitting. The sum of squares of the differences for predicted and experimental ECs was minimized by genetic algorithm implemented by MATLAB R2018. Table 4.2 presents the R-squared values obtained for fitting equations 5-9 to the experimental data. When no C_8H_8 was injected to the biofilter (B-ME), R-squared of 0.99 was achieved. As expressed in Table 4.2, equations 6-9 showed good fitting results of the experimental data with R-squared ranging from 0.89 to 0.99 for simultaneous biofiltration of CH_4 and C_8H_8. The best fit was obtained for uncompetitive inhibition model (equation 7) with R-squared of 0.99, 0.99 and 0.98 for B-200, B-500 and B-700, respectively. The uncompetitive inhibition was confirmed by Albanna *et al*. [21] for bio-oxidation of CH_4 and mixed NMOCs in landfill bio-covers (batch reactors) and Ménard *et al*. [208] for biofiltration of CH_4 and C_7H_8 in lab-scale conventional biofilters.

Table 4.3 presents the macrokinetic parameters of CH_4 biofiltration in B-ME by means of Michaelis–Menten model (equation 5) and for the mixture of CH_4+C_8H_8 in biofilters B-200, B-500 and B-700 by applying the uncompetitive inhibition Michaelis–Menten model (equation 7). In case of CH_4 as the single pollutant (B-ME), $EC_{CH4,max}$ of 311.2 $g.m^{-3}.h^{-1}$ and K_S of 18.76 $g.m^{-3}$ were achieved. In B-200, $EC_{CH4,max}$ of 128.2 $g.m^{-3}.h^{-1}$, K_S of 7.58 $g.m^{-3}$ and K_I of 0.4 $g.m^{-3}$ were achieved. For B-500 and B-700, $EC_{CH4,max}$ of 71.4 and 39.3 $g.m^{-3}.h^{-1}$ and K_S of 5.13

and 2.34 $g.m^{-3}$ were achieved, respectively. No unique values were found for macrokinetic inhibition constant (K_I) for B-500 and B-700 (high ILs of C_8H_8). The same K_I of 0.4 $g.m^{-3}$ was considered for B-500 and B-700 in order to calculate the corresponding $EC_{CH4,max}$ and K_S.

Table 4.2: The R-squared values for curve fitting by means of modified Michaelis-Menten model for macrokinetic study of mixed pollutants in biofilters

R-squared values	Equation	B-ME	B-200	B-500	B-700
Single pollutant	5	0.99			
Competitive inhibition	6		0.97	0.97	0.95
Uncompetitive inhibition	7		0.99	0.99	0.98
Non-competitive inhibition	8		0.99	0.98	0.96
Mixed inhibition	9		0.93	0.90	0.89

Table 4.3: Macrokinetic analysis for CH_4 biofiltration

Macrokinetic parameters					
Second pollutant (inhibitor)		C_8H_8 (styrene)			
Packing material		Inorganic (stone-based)			
EBRT	h	0.1			
IL of inhibitor	$g.m^{-3}.h^{-1}$	-	Low IL	Average IL	High IL
		0 (B-ME)	9 (B-200)	22 (B-500)	32 (B-700)
$EC_{CH4,max}$	$g.m^{-3}.h^{-1}$	311.2	128.2	71.4	39.3
K_S	$g.m^{-3}$	18.76	7.58	5.13	2.34
K_I	$g.m^{-3}$	-	0.4		

To our best knowledge, no macrokinetic study has been reported in the literature for biofiltration of CH_4 and C_8H_8 in a mixture. Ménard *et al*. [208] investigated on the kinetics of CH_4 and C_7H_8 mixture and Streese *et al*. [252] carried out a macrokinetic study for VOCs and odor treatments

in biofilters. Table 4.3 shows the macrokinetic analysis from the present study, which will be compared with the results reported by Ménard *et al*. [208]. $EC_{CH_4,max}$ varied from 311.2 to 39.3 $g.m^{-3}.h^{-1}$ in the present study (C_8H_8 IL of 0 to 32 $g.m^{-3}.h^{-1}$), while a range of 39.4 to 5.6 was obtained by Ménard *et al*. [208] (C_7H_8 IL of 0 to 52 $g.m^{-3}.h^{-1}$). A similar trend was observed for K_S with 18.76 to 2.34 $g.m^{-3}$ for the present study and 4.6 to 0.7 $g.m^{-3}$ for Ménard *et al*. [208]. The disagreement in macrokinetic studies could be due to the experimental operating conditions, i.e. the range of CH_4 IL tested (7 to 60 $g.m^{-3}.h^{-1}$ in the present study and 18 to 82 $g.m^{-3}.h^{-1}$ for Ménard *et al*. [208]) and EBRT (0.100 h in the present study and 0.072 h for Ménard *et al*. [208]). In addition, the second pollutant in two studies were different (C_8H_8 and C_7H_8), which might have affected macrokinetic parameters. The presence of a different NMOC might lead to a different microbial community in the biofilter and could change the biofilter's performance [267, 269]. Macrokinetic inhibition constants (K_I) were 0.6 and 0.4 $g.m^{-3}$ in Ménard *et al*. [208] and the present studies, respectively. The low value of K_I for both studies (Table 4.3) showed that CH_4 biofiltration could be inhibited even at low NMOCs ILs (i.e. C_8H_8 IL of 9 $g.m^{-3}.h^{-1}$ in the present study).

4.6 Conclusion

The performance of elimination of CH_4 only and a mixture of CH_4 and C_8H_8 were investigated. Methane ILs increased from 7 to 60 $g.m^{-3}.h^{-1}$ in 4 biofilters while C_8H_8 IL was kept constant at 0, 9, 22 and 32 g $C_8H_8.m^{-3}.h^{-1}$ in B-ME, B-200, B-500 and B-700, respectively. The CH_4 RE reduced from 80 to 43% for B-ME to B-700. The results revealed the addition of C_8H_8 likely caused an inhibition for CH_4 biodegradation in biofilters treating a mixture of CH_4 and C_8H_8, which led to a lower performance compare with CH_4 biofilter. The lowest CH_4 RE (43%) was obtained at the highest CH_4 IL (60 $gCH_4.m^{-3}.h^{-1}$) and at the highest C_8H_8 IL (32 $gC_8H_8.m^{-3}.h^{-1}$). A C_8H_8 RE of 100% was achieved at C_8H_8 ILs of 9 to 32 $gC_8H_8.m^{-3}.h^{-1}$ in the pseudo steady state due to the high EBRT of 0.1 h of the biofilter. The complete C_8H_8 removal occurred later in B-700 and B-500 (day 90) compared to B-200 (day 60), due to the probable inhibition of MOs, which was originated from higher C_8H_8 IL in B-700 and B-500. The modified Michaelis-Menten model for macrokinetic study of biofilters revealed that most likely, an uncompetitive inhibition led to the decline in average CH_4 RE from B-ME to B-700.

CHAPTER 5 General discussions

In this study, biofiltration of a binary system (CH_4+C_8H_8) was investigated in biofilters working with recycled NS in order to reduce leachate production. For the first time, effects of C_8H_8 in a CH_4 biofilter were investigated. The whole thesis was based on treatment of CH_4 emissions from WWTPs, as the main objective of this study. It was shown that WWTPs and SNWs are important sources of CH_4 and CO_2 emissions. Reports from different locations all over the world revealed that WWTPs and SNWs are among the growing anthropogenic sources of GHG emissions. The current study showed that biofilter is a promising approach to eliminate CH_4 and other gaseous compounds such as VOCs emitting from WWTPs. All efforts to date were related to emissions after sewer discharge into the WWTPs. Since leachate from the biofilter is, itself, considered as wastewater, NS addition strategies were investigated in order to reduce NS consumption. Despite a decrease in the biofilter performance, the current study showed that recycling NS is a reasonable strategy in order to decrease fresh NS utilization, which leads to less leachate production. Biofilters were successfully used to eliminate C_8H_8, a gas that is present in wastewater gaseous emissions. Mixtures of CH_4 and C_8H_8 can also be eliminated in biofilters. The current study showed that periodic starvation periods, high EBRT and packings' type could make the biofilters able to stay active to work efficiently for more than ten months, despite the mass transfer limitations for CH_4 and presence of by-products such as phenolic and catecholic compounds, generated through VOC biodegradation in mixed pollutants biofilters. The macro kinetics of CH_4+C_8H_8 biofiltration were studied and macrokinetic parameters were calculated according to modified Michaelis-Menten model. The low value of K_I showed that CH_4 biofiltration could be inhibited even at low C_8H_8 ILs. A lower value of K_I represents the reduced strength of binding between microorganisms and C_8H_8, a lower inhibition and higher $EC_{CH4,max}$ and K_S. Macrokinetic saturation constant (K_S) as an indicative of MO-CH_4 strength was coordinated with $EC_{CH4,max}$. When interaction between CH_4 and C_8H_8 with microorganisms increased (due to the increased C_8H_8-IL), $EC_{CH4,max}$ and K_S declined. This was proved by an overall decline in CH_4 biodegradation in biofilters. The intermediate C_8H_8-MO-CH_4 reduced MO-CH_4 concentration and slowed down CH_4 biodegradation.

Kinetic models for biofiltration use different assumptions regarding steady-state, transient conditions, mechanisms such as diffusion, dispersion, adsorption and other interactions between

gas (pollutant), liquid (water/biofilm) and solid (biofilm/packing) phases in a biofilter. Nevertheless, all of these models consider the microbial activity. Michaelis-Menten macrokinetic model describes the enzymatic biodegradation in a steady-state biofilter without considering biomass evolution. On the other hand, Monod or Haldane microkinetic models connects the pollutants' biodegradation rate to microbial growth rates for biofilters in both steady-state and transient conditions. The kinetic parameters in models can be experimentally determined, carried out by batch experiments using bacterial strains (pure or isolated from the filtering bed directly). Utilizing biomass samples extracted from the filter bed and directly inserted into the batch reactors can be a solution. Kinetic parameters obtained with batch experiments will be more reliable. Prior operations are needed for sampling the biomass, which means that they might not be a perfect representative of the real growth media (the filter bed). Mass transfer restrictions in the biofilter are not respected in such kinetic models.

In the current study, various concentrations of CH_4 generated from different WWTPs and SNWs were reported. Generally, concentrations of CH_4 higher than 200 g m^{-3} make it feasible to be valorized for energy use purposes, like in anaerobic digesters of WWTPs. The problem is that a large surface in WWTPs is not covered; therefore, low CH_4 concentrations (around 1% v/v) are continuously released into the atmosphere. These kind of emissions are not easy to treat and considered as an important challenge at large scales. Biotechnological treatments such as biofilters are promising and cost-effective compared to physicochemical processes such as incineration and catalytic oxidation, but these bioprocesses for elimination of low concentration CH_4, mainly produced in WWTPs and in sewer biofilms and sediments in rising main and gravity sewers, still need attention. Many aspects of CH_4 biofiltration are still not clear, especially in regards to bioreaction optimization for long-term operations. Future work should focus on modeling the biofilter in regards to parameters affecting the performance. Parameters such as packing material, temperature, moisture and mixed pollutants are usually neglected for biodegradation mechanism and kinetic study and modeling. No global model has been proposed for biofiltration of CH_4 and VOCs/VICs mixtures.

Besides, if a biofilter is used for eliminating gaseous emissions, the wastewater could be used as the nutrients. The nutrients already present in wastewater could supply the need for NS in CH_4 biodegradation. Nevertheless, there will be a problem regarding type and concentration of the nutrient for microorganisms, especially nitrogen sources. Microorganisms prefer NO_3^- as

the nitrogen source, while wastewater may contain nitrite (NO_2^-), which is toxic for CH_4 biofiltration. In addition, microorganisms need certain concentrations of NO_3^- depending on CH_4 IL. In some cases, NO_3^- concentrations in wastewater can reach about 1 gN L^{-1}, which is not suitable for CH_4 biodegradation due to inhibitory effects on microorganisms.

Detailed and comprehensive field data for CH_4 emission from WWTPs and SNWs can give a better perspective for future industrial applications. In addition to eliminate the emissions from wastewater, future work should also consider preventive measures in WWTPs' digesters, with covering the units or adding chemicals to keep CH_4 dissolved in the liquid phase (sewage). On the other hand, even if valorization does not seem feasible for low CH_4 concentrations, future research must consider it for further study in order to use these low concentrations of CH_4 in processes, such as electron donor for water denitrification treatments.

CHAPTER 6 Conclusion

Wastewaters are among the growing source of greenhouse gas (GHG) emissions on earth. Municipal wastewaters and industrial wastewaters lead to methane (CH_4) emissions while being transferred with sewer networks (SNWs) and in wastewater treatment plants (WWTPs). Emissions of CH_4 were reported in different manholes all through the way to WWTPs, no matter if it is a rising main or gravity sewer. The emissions were significant especially in sewer pump stations. Applying cost-effective chemicals and biochemicals to prevent CH_4 formation in wastewater could be useful to decrease GHG emissions. On the other side, the possibility of using the CH_4 emitted from WWTPs as an energy source for the treatment plant itself or domestic energy uses must be also taken into consideration. If no CH_4 valorization is possible, biofilters can be used for elimination of CH_4 emitting from wastewaters, when CH_4 concentration is less than 5% (v/v). Parameters such as packing material, temperature, moisture and CH_4 concentration clearly affect the biofilters' performance in long-term operations. In large-scale practices, presence of volatile organic compounds (VOCs) and volatile inorganic compounds (VICs), which are also emitted from wastewaters, have inhibitory effects on CH_4 biofiltration and cause a decline in biofilters' CH_4 elimination capacity (EC).

Recycling strategy of nutrient solution (NS) is a promising approach to decrease the wastewater production during CH_4 biofiltration. A comparison of using fresh NS (B1) and recycling NS (B2) in CH_4 biofilters showed appropriate performance of B2 with a CH_4 RE of 62% for an inlet load (IL) of 13 g m^{-3} h^{-1}, while B1 showed a CH_4 RE of 66% for a similar IL. Lower RE obtained with the recycling method was related to essential nutrients' consumption (nitrate (NO_3^-) and phosphate (PO_4^{3-})) over time in the recycle tank. Consumption of NO_3^- by the microorganisms was more than other nutrients (i.e. PO_4^{3-} and sulfate (SO_4^{2-})). The performances of biofilters were reliable even without adding NS (in starvation period). After 35 days of NS starvation, CH_4 REs of 55% and 45% for B1 and B2, respectively, were achieved. In comparison with adding 2 L NS per 24 h, a better performance was achieved in B1 and B2 when 0.5 L NS per 6 h was added (total NS amount of 2 L per day), probably due to the adequate time for microorganisms to uptake the nutrients. By means of recycling method, the consumption of NS decreased from 60 L (B1) to 10 L (B2) in 30 days.

The effect of aromatic compounds such as styrene (C_8H_8) during CH_4 biofiltration was studied in 4 parallel upflow biofilters. Methane IL range of 7 to 60 g m^{-3} h^{-1} was adjusted for all biofilters while constant C_8H_8 IL of 0, 9, 22 and 32 g m^{-3} h^{-1} were adjusted in B-ME, B-200, B-500 and B-700, respectively. A CH_4 RE of 76% was achieved in the absence of C_8H_8 in B-ME at CH_4 IL of 60 g m^{-3} h^{-1}, indicating a satisfactory performance. However, at the highest level of C_8H_8 (B-700), a notable CH_4 RE reduction was observed for the same CH_4 IL (CH_4 RE=43%). The addition of C_8H_8 inhibited CH_4 biodegradation and led to a lower performance in mixed pollutant biofilters (B-200, B-500 and B-700) compared to single pollutant (CH_4) biofilter (B-ME). A 100% C_8H_8 RE was achieved due to high empty bed residence time (EBRT) of 6 min in all the biofilters. In general, this study showed that wastewater is an important source of GHG emission (i.e. CH_4) and if valorization of CH_4 is not feasible, biofiltration is a promising method to eliminate CH_4, even in the presence of non-methane organic compounds (i.e. C_8H_8).

6.1 Conclusion in French (conclusion en français)

Les eaux usées font partie des plus importantes sources d'émissions de gaz à effet de serre (GES) sur terre. Les eaux usées municipales et industrielles entraînent des émissions de méthane (CH_4) pendant leur transfert par les réseaux de canalisation (SNW) et dans les stations d'épuration (STEP), causées principalement par la digestion anaérobie. Des émissions de CH_4 ont été signalées dans différentes canalisations tout au long du parcours vers les stations d'épuration. Les émissions étaient importantes, en particulier dans les stations de pompage des égouts. L'application de produits chimiques et biochimiques pour empêcher la formation de CH_4 dans les eaux usées pourrait être utile pour réduire les émissions de GES. D'un autre côté, la possibilité d'utiliser le CH_4 émis par les stations d'épuration comme source d'énergie, pour la station d'épuration elle-même ou pour des utilisations énergétiques domestiques, doit également être prise en considération. Si aucune valorisation du CH_4 n'est possible, des biofiltres peuvent être utilisés pour éliminer le CH_4 émis par les eaux usées, lorsque la concentration en CH_4 est inférieure à 5% v/v. Des paramètres tels que le garnissage, la température, l'humidité et la concentration de CH_4 affectent les performances des biofiltres fonctionnant sur de longues périodes. À grande échelle, la présence de composés organiques volatils (COV) et de composés inorganiques volatils (CIV), également émis par les eaux usées, ont des effets inhibiteurs sur la

biofiltration du CH_4 et provoquent une baisse de la capacité d'élimination (CE) du CH_4 dans les biofiltres.

Le recyclage de la solution nutritive (NS) est une stratégie prometteuse pour diminuer la production d'eaux usées lors de la biofiltration du CH_4. La comparaison dans 2 biofiltres de l'utilisation d'une NS fraiche (B1) ou recyclée (B2) dans des biofiltres de CH_4 a montré une conversion de CH_4 de 62% pour un biofiltre B2 pour une charge d'entrée (IL) de 13 g m^{-3} h^{-1}, tandis que le biofiltre B1 a conduit à une conversion de CH_4 de 66% pour une IL similaire. Les conversions plus faibles obtenues avec la méthode de recyclage étaient liées à la consommation de nutriments essentiels (nitrate (NO_3^-) et phosphate (PO_4^{3-})) au fil du temps dans le réservoir de recyclage. La consommation de NO_3^- par les micro-organismes était supérieure à celle d'autres nutriments (c'est-à-dire PO_4^{3-} et sulfate (SO_4^{2-})). Les performances des biofiltres étaient fiables même sans ajout de NS (en période de privation). Après 35 jours de privation de NS, des conversions de CH_4 de 55% et 45% respectivement pour B1 et B2 ont été atteintes. En comparaison avec l'ajout de 2 L de NS par 24 h, une meilleure performance a été obtenue avec le B1 et le B2 lorsque 0.5 L NS par 6 h a été ajouté (quantité totale de NS de 2 L par jour), probablement en raison du temps nécessaire pour que les nutriments soient absorbés par les micro-organismes. Grâce à la méthode de recyclage, la consommation de NS est passée de 60 L (B1) à 10 L (B2) en 30 jours.

L'effet de composés aromatiques tels que le styrène (C_8H_8) lors de la biofiltration du CH_4 a été étudié en parallèle dans 4 biofiltres à flux ascendant. La plage de CH_4 IL de 7 à 60 g m^{-3} h^{-1} a été augmentée progressivement (7 à 20, 20 à 40 et 40 à 60 g m^{-3} h^{-1}) dans tous les biofiltres tandis que la C_8H_8 IL est restée constante à 0, 9, 22 et 32 g m^{-3} h^{-1} dans les biofiltres B-ME, B-200, B-500 et B-700, respectivement. Une conversion de CH_4 de 76% a été atteinte en absence de C_8H_8 dans B-ME pour une CH_4 IL de 60 g m^{-3} h^{-1}, indiquant une performance satisfaisante. Cependant, en utilisant des niveaux plus élevés de C_8H_8 (B-700), une réduction notable de la conversion de CH_4 a été observée pour la même CH_4 IL (conversion de CH_4 de 43%). Ainsi, l'ajout de C_8H_8 a inhibé la biodégradation du CH_4 et a entraîné une baisse des performances des biofiltres utilisant des mélanges de polluants (B-200, B-500 et B-700) par rapport au biofiltre à polluant unique (CH_4) (B-ME). Une conversion complète (100%) du C_8H_8 a été atteinte grâce à un temps de résidence en fût vide (EBRT) élevé de 6 min dans tous les biofiltres. Finalement, cette étude a montré que les eaux usées sont d'importantes sources d'émissions de GES (c.-à-d.

CH_4) et que si aucune valorisation du CH_4 n'est pas possible, la biofiltration est une technologie prometteuse permettant l'élimination du CH_4, même en présence de composés organiques non méthaniques (c.-à-d. C_8H_8).

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